**US Army Corps
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Waterways Experiment
Station

Installation Restoration Research Program

Review of Formulations for Processes Affecting the Subsurface Transport of Explosives

by   *Christian J. McGrath*

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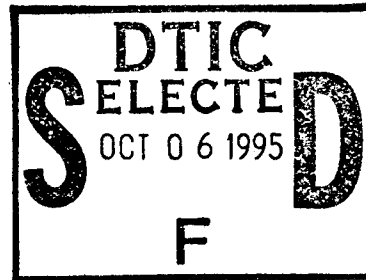
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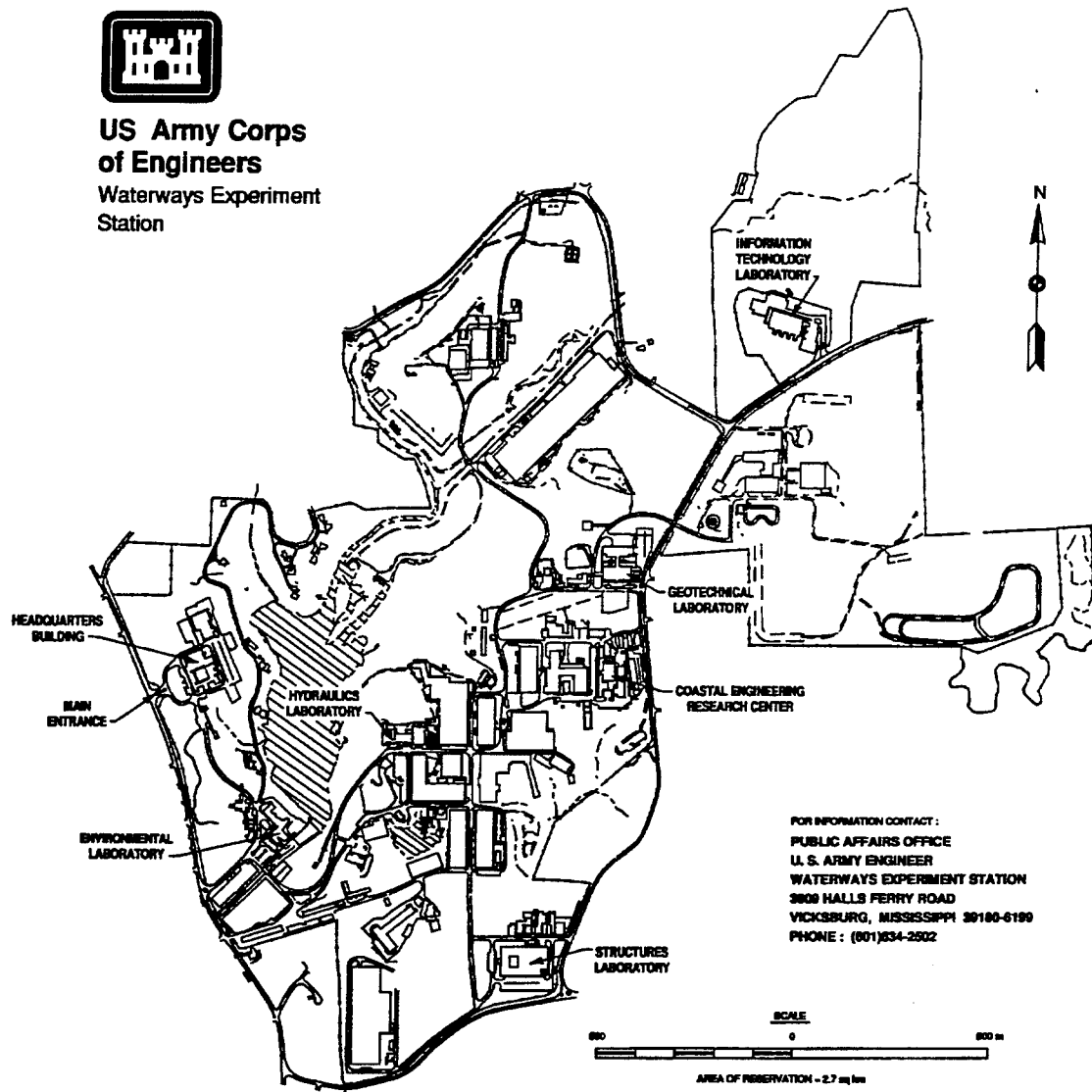3909 Halls Ferry Road
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SCALE

AREA OF RESERVATION – 2.7 sq km

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Preface

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1 Introduction

1.1 Background and Justification

Nature of the problem

Numerous Department of Defense (DOD) installations are tasked with the cleanup of soils and groundwaters contaminated with explosives, propellants, and energetics compounds, as well as a variety of organic solvents, petroleum hydrocarbons, and heavy metals (DOD 1992, Hadala et al. 1993). The focus here is on the migration of explosives in soils, the vadose zone, and aquifers, under varying management and treatment strategies.

The soil environment is the one most commonly affected by explosives wastes, primarily because: (1) spill sites and disposal areas (e.g., burn pits) at packing and production facilities are predominantly in upland areas, and (2) most explosive compounds are solids with low aqueous solubility. Extensive groundwater contamination is associated primarily with wastewater lagoons and leach pits at production and packing facilities.

Numerical modeling has become the most time- and cost-effective, quantitative tool available for the design and optimization of subsurface remediation schemes, particularly for complex in situ technologies. The challenge in numerical modeling is to minimize the numerous sources of uncertainty, such as:

- Identity and relative significance of active processes (particularly true for explosives).

- Level of process coupling (competition, catalysis, etc.).

- Parameter estimations for descriptors (e.g., for reaction or partitioning kinetics) in intrinsically heterogeneous media.

- Error inherent to chemical analysis.

- Scale effects in field sampling, i.e., disparate media volumes are represented by various measurements.

- Total contaminant loading (mass) and history.

- Boundary condition variability.

- Characterization of chemical heterogeneities.

Uncertainty related to the physical structure of the porous medium (e.g., permeability variation) also impedes simulation of subsurface transport, but these limitations are not unique to explosives. These limitations are relaxed somewhat as site investigations proceed and as process research advances. Methods to deal with irreducible levels of uncertainty, such as stochastic modeling, are available, but the topic is beyond the scope of this review.

Numerical models depend upon accurate process descriptors

The predictive output of a numerical model can only be as accurate as the process descriptors upon which the model is based (see Figure 1.1). A process descriptor is a general, mathematical expression that describes the dependence of a predicted value on parameters or properties that can be measured or estimated.

Descriptors can be simple or complex, and always involve implicit assumptions of which the modeler must be keenly aware. For example, a commonly used process descriptor for adsorption is the simple linear isotherm: $S = K_d C$,[1] where S is the adsorbed concentration (sorbate mass/soil mass),
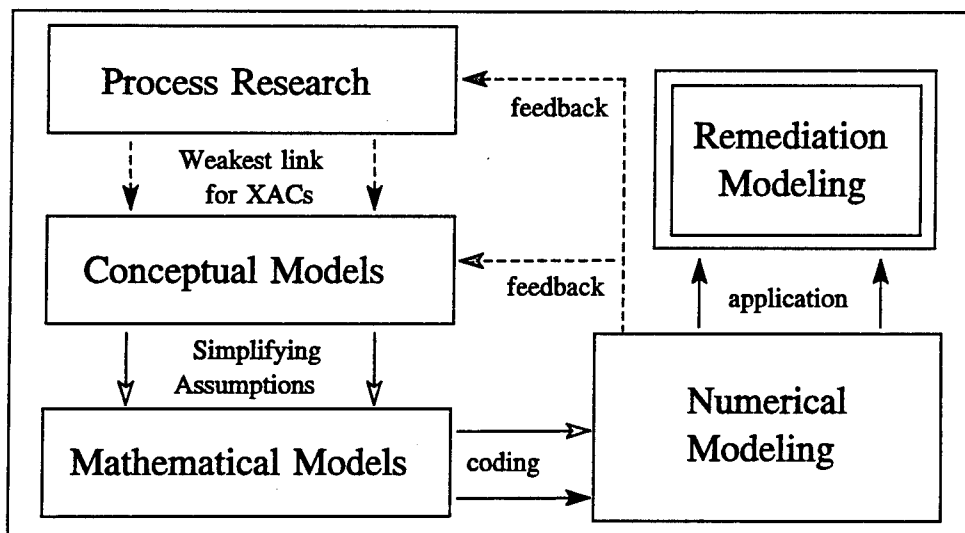
Figure 1.1. Schematic diagram depicting the interdependence of process research, conceptual modeling, and numerical modeling (XAC = explosives-associated contaminants)

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[1] For convenience, acronyms and symbols are listed in Appendix D.

C is the aqueous concentration (solute mass/volume solvent), and K_d is a partitioning coefficient (volume solvent/soil mass). This linear isotherm conceptual model involves several simplifying assumptions: (1) the system is at equilibrium, (2) K_d is independent of concentration C, (3) each solute adsorbs independently, (4) the process is reversible, (5) C is below the solubility limit of the constituent, and (6) S is below the sorptive capacity of the sorbent. Some of these assumptions are commonly invalid (or undocumented) for subsurface contaminant transport, particularly for explosives.

Numerical models are simply software tools with which to calculate approximate solutions to large sets of simultaneous equations. These equations are the mathematical models, which describe the dependence of unknown quantities of interest (e.g., TNT (2,4,6-trinitrotoluene) concentration at some point and time) on known or estimable parameters (e.g., permeability, reaction coefficients, and mass loading). The equations are developed based upon conceptual models derived from laboratory and/or field observations of parameters to be correlated. Numerous simplifying assumptions typically are introduced to make a complex system more tractable numerically. Conceptual models require the informed evaluation of experimental data and may also involve simplifying assumptions as to the complexity of processes, i.e., neglecting processes deemed to be of minor influence. These models are also constrained by chemical principles. Unfortunately, the processes affecting explosives and explosives-associated contaminants (XACs) in the subsurface are poorly understood ("weak link" in Figure 1.1). Numerical simulation provides a feedback mechanism to quantitatively evaluate the validity of process descriptors relative to observations in bench-scale experiments or at field sites.

Appropriate process descriptors are lacking

Process descriptors for explosives are poorly developed because specific reaction mechanisms and their interrelations are poorly understood. Field and laboratory observations strongly indicate that multiple and competing reactions influence XAC transport. The chemical, physical, and biological heterogeneity of the subsurface makes resolution of in situ process exceedingly difficult.

Process descriptors developed for other classes of organics—petroleum hydrocarbons, chlorinated solvents, pesticides—are not adequate to describe XAC transport. XACs are subject to dissolution, sorption, abiotic and microbially mediated reduction reactions, covalent binding to soil components, polymerization, and other reactions. Existing ("off-the-shelf") codes do not begin to approach the complexity that is apparently needed to predict the subsurface fate of explosives wastes.

Simple, individual processes, such as hydrophobic partitioning or the biotransformation of primary substrates, are relatively well understood for the more common contaminants. Data are much more limited for explosives.

Most of the environmental research with explosives compounds has focused on individual processes, primarily sorption and biotransformation. Environmental effects on process rates are poorly known.

Coupled and competing processes pose perhaps the most serious challenge to deciphering XAC behavior. Coupled processes are multiple, simultaneous processes that influence each other directly. Examples of coupled processes that may influence XAC transport or remediation include:

- Desorption kinetics can limit the bioavailability of compounds and therefore transformation rates.

- Excessive, microbial growth can reduce permeability and thus advective transport (biofouling).

- Competition between XAC species for sorption or reaction sites.

Difficulties in studying coupled processes arise: (1) in resolving the processes, and (2) in establishing quantitatively the nature of the coupling. The strength of the coupling has significant bearing on the form of the process descriptor and its numerical solution. Other simultaneous reactions may not be coupled in the strict sense, but are no less difficult to resolve, such as:

- Abiotic versus microbial reduction of nitroaromatics.

- Dissolution of multicomponent solid munitions.

A fast process may obscure a second, but does not necessarily prevent it. The precise nature of competitive and coupled processes remains to be determined for XACs as well as other contaminants.

Process descriptors for new, innovative, in situ technologies potentially useful in the cleanup of XACs are evolving rapidly. Most of these technologies represent an enhancement or manipulation of natural hydrobiogeochemical processes that must be understood well enough to be engineered. Examples of the developing technologies include: enhanced biotransformation by introducing additives (e.g., electron acceptors, substrates, and macronutrients), enhanced solubilization with surfactants, enhanced retardation by cationic surfactant fences, and electrokinetics. Increasingly complex process descriptors, relative to those reviewed here, will certainly be required.

Multiple process descriptors offering a range of complexity are needed in remediation simulation because: (1) a multiple working hypothesis approach will help avoid bias toward a particular process, and (2) the complexity of the descriptors must be commensurate with the level of understanding of the active processes and the site. The multiple hypothesis argument is particularly apropos in light of the considerable uncertainty about processes affecting explosives.

Numerical modeling can be utilized during many stages in the remediation of a contaminated site. The diversity, detail, and amount of site-specific data tend to expand over the life a project. Data availability strongly influences the selection of modeling tools at a given level of characterization of transport processes and site hydrogeology. For example, any preconceptions of simple, hydrophobic behavior for explosives must be abandoned for simulations beyond preliminary screening or risk analysis.

1.2 Goals and Objectives

The primary objective of this report is to review and critically evaluate the information needed to develop process descriptors for the subsurface transport of explosives and XACs. Specific objectives are as follows:

- Identify processes active or potentially active in XAC transport.

- Review existing descriptors for these processes.

- Evaluate applicability of descriptors to explosives.

- Recommend process descriptors to be incorporated into future codes.

- Recommend experimental procedures for future research to elucidate active processes.

This review is intended to generate a set of descriptors, the most promising of which will be incorporated into future groundwater contaminant transport codes specifically designed for XACs. As our understanding of natural and remediation processes affecting explosives evolves in concert with numerical simulation, inappropriate descriptors will be discarded or modified. Improved codes will assist in the quantitative interpretation of bench-scale experiments and ultimately in the evaluation of subsurface remediation alternatives.

An additional objective is to identify and recommend experimental investigations that will be required to resolve alternative conceptual models and determine the necessary parameters for the process descriptors. Experimentation and the development of appropriate mathematical expressions (and their numerical solutions) should be an iterative, synergistic process.

1.3 Approach

This review is necessarily broad in scope because multiple reaction and transport mechanisms are potentially significant in the subsurface transport

of XACs. Abiotic reactions, microbial processes, sorption, and advection-dispersion receive considerable attention because field and laboratory observations indicate that these strongly influence XAC transport. There is no certainty as to which processes are irrelevant, particularly for many of · the breakdown products of explosives.

The general approach adopted for the preparation of this review was:

- Review engineering and scientific literature to identify the nature of explosives contamination at DOD sites.

- Review technical literature to identify multiple processes affecting XACs or surrogate compounds.

- Compile a variety of existing process descriptors and recommend promising descriptors for future code development for XACs.

- Identify the implicit assumptions and requisite parameters for process descriptors and consider their applicability to XACs.

Recommendations for future processes research or laboratory methods are also presented in some cases.

The identity of the XACs of greatest concern was determined by a review of documents and publications describing XAC contamination at several DOD facilities, including facilities for the production, packing, or storing of explosives as well as firing ranges. A wealth of information is available from Army documents prepared under the auspices of the U.S. Army Environmental Center (AEC, formerly the Toxic and Hazardous Materials Agency, THAMA) in support of remedial investigations or feasibility studies at DOD installations. Considerable research on the transport of explosives compounds in surface water has been conducted through the Bioengineering Research and Development Laboratory (BRDL). Two U.S. Army Corps of Engineers laboratories—the Cold Regions Research & Engineering Laboratory (CRREL) and the Waterways Experiment Station (WES)—have investigated various aspects of the environmental behavior of XACs in the soil environment and analytical methods for explosives.

Munitions manufacturing facilities at Louisiana Army Ammunition Plant (LAAP) and Cornhusker Army Ammunition Plant (CAAP) were examined to identify typical scenarios that may be encountered in explosives remediation. Information on the relative frequency and distribution of explosives compounds at these facilities provides an appreciation for the net effects of processes in groundwaters.

None of the process descriptors extracted from the literature and reviewed here were developed specifically for explosives. This fact reflects the limited research into the fundamental processes affecting XAC

fate and transport and raises reasonable doubts about the applicability of existing descriptors to explosives. The reviewed descriptors are distilled from a vast technical literature related to soil and groundwater contaminant transport. No single report (or author) could hope to review all contributions to this multidisciplinary field. Review of investigations of simpler nitro- or amino-aromatics, pesticides, and dyes, as well as explosives, provided the basis for identifying the key processes involved.

Processes affecting the fate and transport of explosives in surface environments (soil, plants, and surface water) have been extensively reviewed (Spanggord et al. 1980a,b, 1982a,b; Spanggord and Suta 1982). The information in these reports provided useful guidance as to the appropriate emphases in this review of subsurface processes. However, process descriptors and parameters developed for well-mixed, open water systems are not necessarily applicable to the subsurface environment without revision.

Numerical methods per se are not reviewed. Numerical modeling techniques are available to solve virtually any set of partial differential equations likely to be encountered in solute transport modeling, though this solution may not be a trivial exercise. The two areas of much greater uncertainty are (1) the reaction mechanisms and their descriptors, and (2) subsurface characterization in terms of chemical and physical heterogeneity.

1.4 Report Organization

Processes are reviewed within six, broad categories—advection, dissolution, sorption, volatilization, biotransformation, and abiotic reactions— discussed in Chapters 3 through 8, respectively. Descriptors for coupled processes (two or more interacting processes) are reviewed in the chapter on only one of the involved processes, with minimal reference in the other(s). For example, the effect of adsorption on biotransformation is discussed in the biotransformation chapter and mentioned briefly in the sorption chapter.

Chapter 2 provides an overview of explosives chemistry for the uninitiated. The types of XACs and their environmental behavior are introduced by examining two cases of groundwater contamination by XACs (Section 2.1). The unusual environmental behavior of XACs ultimately depends on their molecular structure. A brief overview of nitroaromatic and nitrogen-heterocyclic molecular structure and properties (Section 2.2) is presented to provide some background material.

Chapter 3 is a discussion of advection, dispersion, and diffusion. Advective transport is certainly the primary mechanism for the dispersal of solutes away from a source area. Flow and advection in seasonally frozen ground are reviewed in an associated CRREL document (Grant 1995).

Chapter 4 presents a short review of aqueous solubility and dissolution kinetics. Very little work has been done on dissolution kinetics of explosives, particularly from multicomponent mixtures.

Chapter 5 is an extensive review of adsorption processes. Equilibrium and nonequilibrium (both chemical and physical) processes are reviewed.

Chapter 6 is a short overview of the volatilization process. Though explosives are considered nonvolatile, some XACs are moderately volatile. Mass transfer at the water-vapor interface (water table or residual water in vadose zone) may prove to be important for small molecular weight XACs and/or electron acceptors (e.g. oxygen for aerobic bioreactions).

Chapter 7 is an extensive review of microbial processes. XACs are unquestionably susceptible to biotransformation. Unfortunately, field scale investigations rarely monitor the transformation products of TNT or RDX. Growth kinetics and biotransformation kinetics of primary and secondary substrates are reviewed. XACs tend to be biotransformed as a cometabolite in most cases, though mineralization by certain microbial consortia is reported.

Chapter 8 includes reviews of several, abiotic processes: hydrolysis, photolysis, aqueous speciation, and abiotic reactions. The emphasis is on abiotic reactions—reduction, polymerization, and binding—by far the most relevant for subsurface transport modeling.

Chapter 9 presents a summary and conclusions of this report and recommendations for future research.

An extensive list of references is presented after Chapter 9 followed by several appendixes:

- Appendix A: Physical, Chemical, and Environmental Data.

- Appendix B: Solubility Correlations.

- Appendix C: Glossary.

- Appendix D: Notation.

The data summary tables (Appendix A) are considered "living" documents, since data gaps are large in many cases. Contributions from interested readers are welcome.

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2 Introduction to Explosives' Chemistry and Hydrogeology

Some fundamental concepts in hydrogeology, contaminant transport, and the chemistry of explosives-associated compounds (XACs) are reviewed in this chapter. Subsequent discussions of individual processes will draw on these concepts.

The overview of the chemistry of explosives and associated compounds (Section 2.1) lays the foundation for understanding the fascinating and complex environmental behavior of XACs. The various types of XAC source areas that have affected groundwater quality are reviewed briefly in Section 2.2. Examination of the groundwater transport of XACs at two Army ammunition plants (AAPs) provides a field-scale perspective of important processes (Section 2.3). Finally, fundamental hydrogeologic concepts are reviewed in Section 2.4, particularly with respect to chemical and physical heterogeneities and their impact on contaminant transport.

2.1 Chemistry of Explosives and XACs

The composition and structure of any compound are the fundamental controls of its physical properties and chemical reactivity under a given set of environmental conditions. This primer on the chemistry of explosives and XACs is presented to (1) relay some fundamental concepts in organic chemistry—structural terminology, key reaction mechanism, etc.—drawn upon in subsequent discussions, and (2) help the reader develop an appreciation for the complexities in XAC fate and transport process research and numerical modeling thereof.

XACs include military high explosives (e.g., RDX, HMX, TNT), a multitude of production waste compounds (e.g., excess reactants, undesired isomer products), and a still wider array of transformation products from photolytic, biotic, and abiotic reactions (see Appendix D for acronyms). Additionally, munitions require a number of additive compounds (e.g., stabilizers,

oxidizers, triggers) which have their own production wastes and degradation products. Conservatively, there are hundreds of XACs that could occur as groundwater contaminants.

Field investigations at XAC-contaminated sites traditionally focus on delineating the extent of plumes of the major explosives (most often TNT and/or RDX) and a limited suite of associated contaminants. This limited focus is appropriate for a cleanup mission. However, the resulting incomplete picture impedes the drawing of conclusions regarding reaction mechanisms or rates. The focus on major contaminants is partially due to the availability of pure compound and relatively well developed analytical procedures. Quantitative, chemical analysis for XACs is difficult, particularly for some of the more exotic transformation products for which no pure compound is available (or is prohibitively expensive) with which to prepare analytical standards.

The XACs of primary interest here may be broadly classified as nitroaromatics (e.g., TNT), aliphatic, nitro-azines (N-heterocyclics; e.g., RDX), and their major amino-, azo-, and azoxy-transformation products (see Figure 2.1 and the Glossary in Appendix C). A minimal number of compounds are discussed that will relay the key structures and processes potentially affecting XAC transport.

Chemistry of carbon, nitrogen, and nitrogen compounds

The molecular structure of some representative XACs and the potential influence of structure on environmental fate are reviewed here. A brief review of carbon and nitrogen chemistry will provide a basis for understanding the environmental behavior of nitrogen-bearing organic compounds.

XACs are organic chemicals (or simply organics), which by definition are comprised predominantly of carbon (C) and hydrogen (H). Of course, other elements are present in organics—predominantly oxygen (O), nitrogen (N), phosphorus (P), and trace amounts of many others. Synthetic, halogenated organic compounds are common industrial solvents, chlorine (Cl) being the most common halogen used. Key elemental properties for C, N, O, and H are summarized in Table 2.1.

The valence of an atom refers to the number of electrons the atom has accepted or contributed in bonding interactions to attain its configuration, the most stable being full orbitals with no unpaired electrons. A negative valence indicates that the atom has accepted additional electrons (a reduced condition) in excess of its atomic number (number of protons); a positive valence indicates that electrons have been donated or contributed to a bond relative to its atomic number. An atom is reduced if the valence decreases (more negative or less positive) as a result of a reaction; conversely, it is oxidized if valence increases.

Geochemical modeling of systems susceptible to oxidation-reduction
(redox) reactions requires careful bookkeeping of electron transfers—some
measure(s) of electron activity such as pe is a primary (or master) variable.
The redox sensitivity of nitrogen suggests that careful attention be given to the
redox condition in a system involving nitroaromatic XACs, which are subject
to both abiotic and microbially mediated, nitro-to-amino reduction reactions.
Redox reactions are discussed more fully in Chapters 7 (Biotransformation)
and 8 (Abiotic Processes).

Carbon (atomic number = 6) has six electrons, forming four sp^3 hybrid
orbitals, each with a single electron. Thus, carbon tends to form four cova-
lent bonds (shared electrons) in an approximately tetrahedral arrangement.
The most common valence for carbon is negative four [-IV], e.g., methane,
CH_4. Single bonds are also called σ-bonds. Carbon may form double bonds
in which two of the sp^3 electrons shared with another atom. Hydrogen, with a
single electron (valence [+I]), tends to form a single covalent bond. Oxygen
(common valence of [-II]), with two unpaired sp^3 orbitals with unpaired elec-
trons, tends to form two bonds (Morrison and Boyd 1983). Table 2.1 summa-
rizes the XAC element characteristics.

Table 2.1
Summary of Major XAC Element Characteristics

Element		Atomic Mass $(g \cdot mol^{-1})$	Number of Orbitals with Unpaired Electrons[1]	Common Elemental Valences[2] (and example[s])
Carbon,	C	12.011	4 sp^3	-IV (CH_4)
Nitrogen,	N	14.007	3 sp^3	-III (NH_3; NH_4^+) 0 (N_2) +III ($Ar-NO_2$; NO_2^-) +V (NO_3^-)
Oxygen,	O	15.999	2 sp^3	-II (H_2O; as above)
Hydrogen,	H	1.008	1 s	+I (as above)

[1] See Morrison and Boyd (1983) for discussion.
[2] Ar: generic symbol for an aromatic hydrogen-carbon structural unit (e.g., benzene ring).

Nitrogen (N) has five valence electrons, also forming four sp^3 orbitals.
However, only three of the orbitals contain unpaired electrons. Thus, nitro-
gen tends to form three single bonds in a slightly flattened tetrahedral arrange-
ment with N and the paired electron orbital at the apex (Morrison and Boyd
1983). Valence may be between [+V] and [-III], but the valences [+III] (e.g.,
$Ar-NO_2$) and [-III] (e.g., $Ar-NH_2$) are most often encountered in XACs.

Electronegativity is a numerical indicator of an atom's or a molecular component's capability to attract electrons; larger values indicate a stronger attraction. As a general rule, elements at the upper right corner of the periodic chart are most electronegative (e.g., F = 4.0), decreasing to the left and down the chart (e.g., K = 0.8). Nitrogen (3.0) is more electronegative than carbon (2.5) and phosphorus (2.1), but less electronegative than oxygen (3.5). The nitro functional group ($-NO_2$) is relatively electronegative and thus tends to draw electrons from adjacent structures, such as from the π-orbitals of an aromatic ring. Methyl ($-CH_3$) and amino ($-NH_3$) groups are weakly electronegative and may tend to push electrons away. The presence and position of these electron drawing and pushing groups may account for some of the differences in behavior between aromatic XACs (TNT, DNTs, amino-DNTs) and nitro-azine XACs (RDX, HMX). These locally polarizing effects may influence the specific interactions with functional groups in soil organics, even for symmetrical molecules (e.g., TNT) which are ostensibly nonpolar. The relative susceptibility of organics to biotransformation is also influenced by the positions of structural components.

The benzene ring (see Figure 2.1, item 1) is the base structure for any nitroaromatic XACs with a toluene or benzene root name. Each of the six carbons binds one hydrogen, oriented radially from the planar ring structure. The other three binding electrons are involved in carbon-carbon bonds: two in σ-bonds to adjacent carbons, the third shared in a delocalized π-bond. The six π electron orbitals essentially merge to form a doughnut-shaped orbital on either side of the ring. The π-bond instills a significant rigidity and chemical stability to the benzene structure (Morrison and Boyd 1983).

Cyclic hydrocarbons (Figure 2.1, items 2 and 3) form a ring but without the delocalized electrons of the π-bond. Each carbon is bound to two others in the ring, and to two hydrogens. Such compounds will be referred to generally in this report as aliphatic rings or simply ring compounds. If an atom other than carbon is present in the ring structure, the molecule is broadly classified as heterocyclic. Aromatic heterocyclics (e.g., pyridine; see Figure 2.1, item 4) are not commonly encountered among XACs. Nonaromatic (cyclic), nitrogen-heterocyclic compounds include RDX, HMX, and related compounds.

The nitro functional group ($-NO_2$) is a common moiety in explosives. The relatively strong electronegativity of the nitro group and its susceptibility to reduction reactions have important repercussions in terms of its interaction with other solutes or soil components (electron donors). The amino functional group ($-NH_2$) is very common in the transformation products of explosives; it is much less electronegative than a nitro group. Ammonia ($N[-III]H_3^0$) and ammonium ion ($N[-III]H_4^+$) are sometimes associated with explosives production wastes. Amino groups of XACs may also ionize, though very little data are available on the environmental behavior of amino-nitroaromatic compounds. Much of the subsequent discussion will revolve around the reduction of nitro groups to amino groups ($Ar-NH_2$) in explosives.

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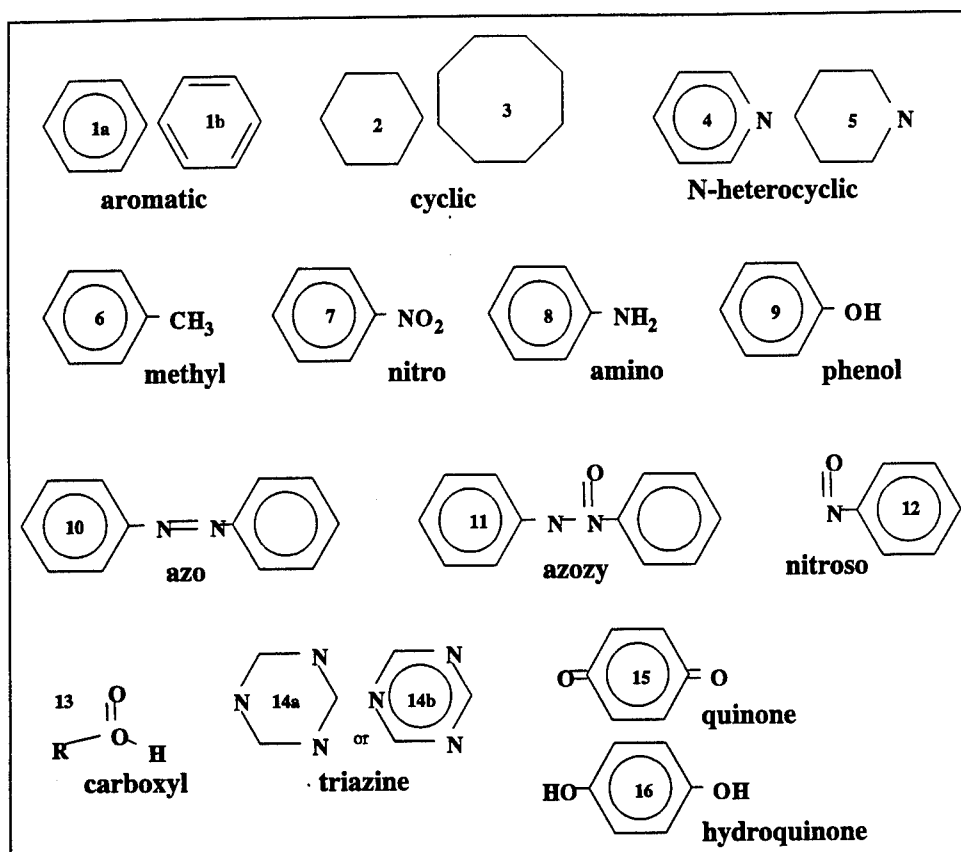
Figure 2.1. Primer on organic compound molecular structure. Key: 1 = benzene (a and b represent two, common depictions of aromicity); 2 = cyclohexane; 3 = cyclooctane; 4 = pyridine; 5 = N-cyclohexane (note that 2, 3, and 5 are aliphatic rings, which do not share π-electrons as do 1 and 4); 6 = toluene; 7 = nitrobenzene; 8 = aminobenzene or aniline; 9 = phenol; 10 = azobenzene; 11 = azoxybenzene; 12 = nitrosobenzene; 13 = carboxyl group; 14a = cyclic triazine and 14b = aromatic triazine; 15 = quinone, 16 = hydroquinone. The R is a generic symbol for an organic, structural group (aromatic, aliphatic)

The methyl functional group (–CH$_3$) is present in many XACs. Toluene, or methyl benzene, is the central structural entity for TNT and associated cocontaminants. The weakly electronegative methyl group "pushes" the π electrons of the aromatic ring. Azo and azoxy compounds (Figure 2.1, items 10 and 11) can form by anaerobic polymerization reactions of amino-bearing compounds.

Specific interactions between XAC functional groups and the carboxyl groups (Figure 2.1) in soil organics (humic/fulvic acids) have been reported. Quinones and hydroquinones (Figure 2.1) have been identified as possible mediators of the nitro-to-amino reduction reactions.

XAC physicochemical properties

Chemical characterization of the majority of the XACs, particularly the environmental transformation products, is impeded by the limited availability of pure compounds. Thus, most of the discussion here focuses on the better characterized XACs such as the explosives and some of the amino derivatives.

The high explosives compounds of interest in this review may be characterized generally as nitroaromatic or nitrogen-heterocyclic compounds and their alteration products. The physicochemical properties that have bearing on subsequent discussion of environmental fate and transport are described broadly below and tabulated specifically in Appendix A for RDX, HMX, 2,4,6-TNT, 2,4-DNT, 2,6-DNT, 1,3,5-TNB, 1,3-DNB, and tetryl (see Table 2.2 for chemical names).

Explosive nature. The utility of explosives lay in the strongly energetic and exothermic reaction initiated upon detonation or ignition. Most modern explosives are reasonably stable and require percussive shock or other triggering devices for detonation. Fortunately, subsurface XAC contamination usually occurs as dilute, aqueous solutions and thus presents no explosion hazard. However, masses of pure crystalline explosive material have been encountered in soils associated with wastewater lagoons, leach pits, burn pits, and perhaps firing ranges. These materials remain hazardous for long periods of time and must be removed by specialists.

Molecular structure. Explosives contaminants are primarily nitroaromatics (TNT-associated) or nonaromatic, nitrogen-heterocyclic (ring), nitroazines (RDX-associated) compounds with methyl $(-CH_3)$, nitro $(-N[+V]O_2)$ functional groups. Most of the explosives compounds to be discussed here are nonionic and only slightly polar (see Appendix A for representative dipole moments). Molecular weights are moderate, ranging from 168 $g \cdot mol^{-1}$ (DNB) to 296 $g \cdot mol^{-1}$ (HMX). Two-dimensional, molecular structure diagrams of representative explosives are presented in Figure 2.2 and Appendix A.

The molecular structure, particularly the type and position of subsidiary functional groups, is the root control on environmental behavior. For example, Chou and Spanggord (1981) report that relative positions of the nitro groups affect TNT biotransformation rates with nitros in the para position (e.g., 4 in 2,3,4- and 2,4,5-TNT) most susceptible to degradation by several surface water microbial consortia. Meta position nitro groups (e.g., 3 and 5 in 3,4,5-TNT) were most stable, while those in the ortho position (e.g., 2 and 6 in 2,4,6-TNT) were intermediate.

Melting points. All of the common, explosives materials are solids at environmental temperatures and pressures. Melting point temperatures for explosives solids are moderate (50-205 °C). Melting points per se are of little direct value in predicting environmental fate and transport, but several parameter estimation relations for solids incorporate the influence of molecular crystal bonding by incorporating a term dependent on the melting point. Melting

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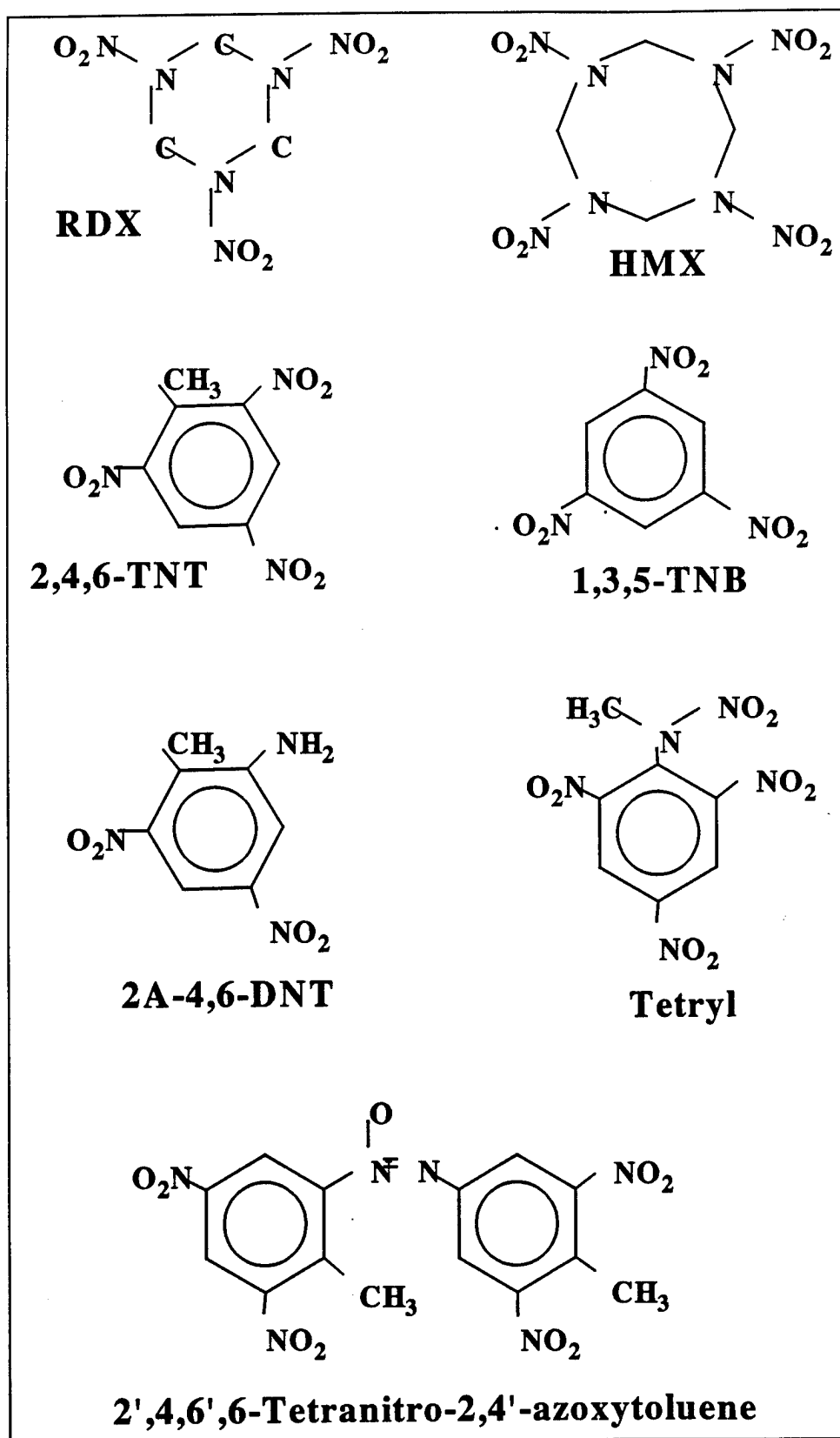
Figure 2.2. Molecular structures for a representative suite of explosives and associated compounds

points for common explosives are known, but are not available for many of the breakdown products.

Volatility. Most of the explosives and associated contaminants have very low volatility, with vapor pressures estimated to be less than 6×10^{-4} torr. Volatilization from the solid phase (sublimation) and solute volatilization are discussed briefly in Chapter 6. Henry's law constants (K_H) range from 10^{-4} to 10^{-11} atm·m^{-2}·mole^{-1}. Only those with K_H greater than approximately 10^{-5} volatilize significantly from aqueous solution (Thomas 1990a). Though explosives compounds may not be volatile, some of the transformation products, other key reactants, or products may be volatile to semivolatile.

Aqueous solubility. Most explosives and XACs are sparingly soluble in pure water, typically less than 200 mg·L^{-1} at 25 °C (see Chapter 4). The aqueous solubility of explosives, like many solid compounds, exhibits a direct temperature dependence (see Tables A1-A7).

Sorption. Sorptive processes are among the most important affecting XACs transport in the subsurface, as discussed in Chapter 5. Reversible partitioning of explosives solutes onto soil and aquifer solids is moderate, much less than for classic hydrophobic organic solids (e.g., some PCBs, pesticides). Partitioning of XACs to soils material varies considerably. K_ds on the order of 1 to 3 are reported for RDX; TNT has reported K_d's in the range of 2 to 56. Larger, polymerized XACs (e.g., azo compounds) are likely to be much more hydrophobic. Sorption characterization of certain XACs is complicated by their irreversible, covalent binding to soil components.

Octanol-water partitioning coefficients, $K_{o/w}$, a relative indicator of hydrophobic partitioning, range over at least two orders of magnitude for XACs, from a low 1.15 for HMX to over 100 for TNT and 2,6-DNT. The organic carbon partitioning coefficient (K_{oc}) is an indicator of a compound's propensity to adsorb to soil organics by hydrophobic partitioning. K_{oc}s for explosives range from very low (3.47 for HMX) to significant (525 for TNT). The apparent inconsistency of low aqueous solubility and the tendency not to partition out of solution is likely the result of stronger intermolecular bonds within the crystalline structure (note that HMX and RDX have relatively high densities; Tables A1 and A2). Empirical correlations between solubility and octanol/water partitioning coefficients derived from saturated hydrocarbons or highly halogenated hydrocarbons data should be applied to nitroaromatics only tenuously.

Biodegradability. Biodegradation is certainly one of the more significant processes affecting the fate of explosives in the subsurface. Most XACs are susceptible to microbially mediated biotransformations. At least partial mineralization of several explosives compounds (e.g., TNT, RDX) has been reported under controlled conditions, usually by cometabolic processes, i.e., the explosive is not the primary, microbial carbon or energy substrate (Kaplan 1993). There are a few reports of microbes growing exclusively on

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explosives. Subsurface biotransformations appear to be incomplete and slow without direct stimulation such as flooding with nutrients. Many questions with respect to optimal degradation pathways and controls on kinetics require elucidation before in situ bioremediation of explosives approaches implementation. On the other hand, tremendous opportunities exist for the development and application of innovative, bioremediation technologies applied to DOD sites.

Toxicity. Virtually all of the XACs are considered hazardous materials and several are known or suspected human carcinogens (e.g., 2,4-DNT). Rosenblatt et al. (1989) present an overview of the aquatic and mammalian toxicology of explosives. This subject is not addressed directly in this report.

Parameter estimation. Groundwater models for XAC transport require at least reasonable estimates of key transport parameters. Many of these parameters simply are not available for XACs, particularly the transformation products. Experimental determination of transport parameters is preferable, but is not always feasible due to scarcity or nonavailability of the pure compound needed for research and quantitative analysis. One alternative approach is to estimate the environmental behavior of poorly known compounds based on correlations established between the known properties of compounds with similar structure and/or functional groups. These quantitative structure-property relationships (QSPRs) and quantitative structure–activity relationships (QSARs) have proven useful for many contaminants. Application of QSPR to XACs has been limited. Explosives are sufficiently unique compounds to merit the development of QSPR based solely on XACs and compounds of similar structure. Banerjee, Yalkowsky, and Valvani (1980) included RDX in the database for defining an aqueous solubility—octanol/water partitioning QSPR for hydrophobic organics. They indicated that special consideration is needed when mixing data from solid contaminants with those for liquids in the same QSPR. A thorough discussion is beyond the scope of this report, but the QSPR holds promise for application to XACs for which experimental data are unavailable.

2.2 Sources of Explosives Contamination

The XACs may enter the subsurface from several, general types of sources: (1) production facilities, e.g., wastewater lagoons, filtration pits; (2) solid waste destruction facilities, e.g., burn pits, incineration wastes; (3) packing or warehouse facilities; and (4) dispersed, unexploded ordnance, e.g. on firing ranges. These sources and modes of XACs discharge represent potentially unique suites of contaminants, each transformation reflecting a unique initial composition and suite of transformations prior to infiltration. Source areas would be represented in numerical simulations as point loadings or areal transport boundary conditions.

Wastewaters from manufacturing and packing operations have posed the greatest threat to groundwaters. These wastes are introduced to the subsurface

in the aqueous phase by leakage from wastewater lagoons, in which the XACs are subject to photolytic and microbially mediated reactions. The other source types are primarily solid wastes in soils from which the contaminants must be leached or dissolved. Since most solid XACs are sparingly soluble in water, their loading rate to groundwaters is likely to be lower than from contaminated, ponded water. The major contaminants in explosives and energetics waste streams, many of which have been identified in groundwaters, are summarized in Table 2.2.

Manufacturing and processing facility wastewaters

Wastewaters from explosives manufacturing typically contain a complex mixture of nitroaromatic, azo-, and azoxy-compounds (Spanggord et al. 1982a, Rosenblatt et al. 1989; see Figure 2.1). Spanggord and Suta (1982) conducted a reconnaissance survey of a TNT manufacturing facility, collecting samples at several points along the waste stream, including the wastewater storage pond, so as to establish qualitative correlations between observations and suspected processes. Even the "fresh" waste stream effluent contained traces of photodegradation products, indicative of the sensitivity of TNT to photooxidation.

Identifying wastewater contaminants provides one survey of compounds that might enter or have already leaked into the subsurface. Spanggord et al. (1982a) and Spanggord and Suta (1982) identify over 30 nitroaromatic compounds in the waste stream of a TNT production and purification facility, including the following (the number in parentheses refers to the number of isomers identified):

- Nitrotoluenes: mono- (3), di- (6), and tri- (3)

- Aminodinitrotoluenes (8 of 16 isomers observed)

- Nitroxylenes

- Nitrobenzonitriles

- Nitrophenols

- Nitrated benzenes

All six dinitrotoluenes are detected with over a 70 percent occurrence rate in the waste stream. The 2,4-, 2,6- and 1,3- isomers were consistently the major effluent components (75 percent by mass). The "red water" of TNT production is an aqueous solution of dinitrotoluenesulfonate salts produced in the sellite purification process by which the asymmetric TNT isomers (other than 2,4,6-TNT) are reacted with sodium sulfite. These wastes are generally concentrated and incinerated.

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Table 2.2
Partial List of XACs Identified in Manufacturing Waste Streams, Wastewater Lagoons, or Contaminant Plumes[1]

Compound(s)	Abbreviation	Comments
TNT-Associated Compounds		
2,4,6-trinitrotoluene	TNT or 2,4,6-TNT	Historically, most important high explosive in U.S.; widely used
2,5,6-trinitrotoluene and other isomers	2,5,6-TNT et al.	One of 6 TNT isomers; asymmetric TNT byproducts removed
2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-dinitrotoluene	2,3-DNT, ..., 3,5-DNT	Impurities in TNT; 2,4- & 2,6- isomers are most common in waste streams and low-melting mixtures
1,3,5-trinitrobenzene	TNB	Photolytic alteration of 2,4,6-TNT (oxid., decarbox.) or impurity in TNT; photolysis product
1,3-dinitrobenzene	1,3-DNB	Alteration of 2,4- or 4,6-DNT or byproduct of TNT
2-amino-4,6-dinitrotoluene, 4-amino-2,6-dinitrotoluene	2-A-4,6-DNT, 4-A-2,6-DNT	TNT nitro-to-amino reduction reaction products
2,4-diamino-6-nitrotoluene, 2,6-diamino-4-nitrotoluene	2,4-A-6-NT, 2,6-A-4-NT	Further nitro-to-amino reduction reaction products from mono-amino compounds
RDX-Associated Compounds		
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	Currently, the most important military high explosive in U.S.; RDX = Research Department or Royal Demolition eXplosive
Octahydro-1,3,5,7-tetra-nitro-1,3,5,7-tetrazocine	HMX	Propellant; acceptable production impurity; HMX = High Melting Explosive or Her Majesty's eXplosive
1-acetylhexahydro-3,5-dinitro-1,3,5-triazine	TAX	Impurity in RDX manufacture
1-acetylhexahydro-3,5,7-trinitro-1,3,5,7-tetra-zocine	SEX	Impurity in RDX manufacture
Miscellaneous Munitions-Associated Compounds		
N,2,4,6-tetranitro-N-methylaniline	Tetryl	Booster explosive; use largely superseded by RDX
Ammonium picrate, picric acid	AP, PA	
[1] Adapted from Rosenblatt et al. (1989) and Spanggord et al. (1982a)		

Leachates associated with incineration wastes, burn pit soils, and filtration ponds have been identified. The solids composition in these wastes would likely depend on the nature and completeness of the burning process. The burn wastes are generally poorly characterized; very little data are available.

Although TNT is a widely used military explosive, it is no longer manufactured in the United States. Crystalline XACs are, however, very persistent in soils, so continue as a contaminant source long after production has ceased.

Large chunks of explosives present a detonation hazard. New environmental releases are more likely associated with packing/storage facilities or unexploded ordnance.

RDX is presently the most important, military, high explosive in the United States (Rosenblatt et al. 1989). The acronym is the British code name for Royal Demolition or Research Department eXplosive. Ordnance of pure RDX is referred to as Composition A; blended with 40 percent TNT it is Composition B.

Packing or storage facilities

Soil and groundwater contamination from packing and storage facilities would be a distinctly different problem. Here the contaminant source is a relatively well-defined mixture of microcrystalline explosives that are sparingly soluble in water at environmental temperatures. The source material is spread locally across a soil surface by unintentional release. The composition of material subject to dissolution and percolation into soils is likely to be that of the ordnance, primarily RDX and TNT. Little data are available concerning environmental alteration of solid phase explosives. Although aqueous solubility data are available for many explosives, dissolution kinetics data for pure or mixed solids are not available.

Wastewaters at packing facilities result from the washing of explosives from shells. The wastewaters were discharged to storage lagoons where dissolved explosives were subject to photolytic and biotransformation reactions. The transformation products caused a pink discoloration of the water, thus the informal term "pink water" for such wastes.

Unexploded ordnance (UXO)

Unexploded ordnance (UXO; a.k.a. ordnance explosive wastes or OEW) represents a problem similar to that of packing facility discharges in that the explosive compounds released are relatively pure, crystalline solids. The environmental release of explosives from UXO would require either that the casing be broken, perhaps upon impact, or that not all of the explosive was burned upon detonation. In either case the source material would be dispersed in a spotty pattern that would be difficult to specify for modeling purposes.

2.3 Examples of Groundwater Contamination

Field observations of explosives and XACs at contaminated sites provide some useful insights regarding the net effect of multiple processes on XAC

fate and transport in the subsurface. Most investigations of XAC-contaminated soils and groundwaters have been geared toward remediation; elucidating details of attenuating processes is typically a secondary priority. This fact is not surprising considering that an effective, field sampling protocol would require some fundamental understanding of the processes affecting XACs transport—that understanding is rudimentary at present. Any improved process descriptors or numerical modeling tools must ultimately be applicable at the field scale.

Explosives and XACs have been detected in the soils and/or groundwaters at numerous Federal facilities for which the DOD is responsible. The Louisiana Army Ammunition Plant (LAAP) and the Cornhusker Army Ammunition Plant (CAAP) were selected as representative examples because groundwater contamination has been reported as extensive. Site characterization and XAC monitoring data are reasonably complete for these installations. Groundwater flow and XAC transport modeling has been attempted at both sites. These two cases provide a frame of reference for the process descriptor review in that the waste suites, hydrogeologic settings, and limited site characterization data are typical situations.

Louisiana Army Ammunition Plant (LAAP)

LAAP is a munitions loading and packing facility in northwest Louisiana operating since 1942. The explosives compounds RDX, HMX, TNT, DNTs, TNB, and tetryl have been detected in mappable plumes associated with numerous sites, including loading areas, wastewater lagoons, landfills, burning grounds, etc.

The near surface geology has a rather complex stratigraphy of Pleistocene, fluvial terraced deposits (basal gravels fining upward to clays; 0-46 m (0-151 ft) thick), underlain unconformably by Eocene, nonmarine, massive sands, silty sands, silty shales, and sparse lignitic beds. The key point here is that these heterogeneous, unconsolidated, sedimentary units of interbedded sands, silts, and clays are not at all unusual, and may typify the subsurface media that must be dealt with in remediation and modeling.

Data from the late 1980's indicate that the explosives had entered both terrace aquifers beneath a cluster of "pink-water" discharge lagoons (Area P). XAC plumes had not advanced very far laterally, suggesting either a strong attenuation mechanism (sorption, binding, transformation) or very slow advective transport in the local very fine-grained sands and silts.

Groundwater transport of TNT, RDX, and DNBs from six sites within the installation was modeled recently by Engineering Technologies Associates, Inc. (ETA 1991a,b). ETA applied a modified version of the U.S.G.S., modular, three-dimensional groundwater flow code *MODFLOW* (MacDonald and Harbaugh 1988). XAC transport was modeled with *RAND3D*, modified from Prickett's two-dimensional, *RANDOM-WALK* model (ETA and Prickett &

Assoc. 1989). The modeling effort was undertaken as a risk analysis screening with minimal site-specific data to support a detailed transport code.

Many simplifying assumptions were made for this screening effort. Sorption is treated as an equilibrium, linear, reversible reaction, permitting the application of the retardation factor concept (see Chapter 5). Though the *RAND3D* model permits first-order decay, no transformation is considered. Considerable parameter uncertainty, particularly as related to sorption behavior, was dealt with by conducting sensitivity analyses. Model results predicted plume migration to the east. Ongoing WES research at the LAAP will further investigate the nature of the heterogeneities and their effect on XAC transport.

Cornhusker Army Ammunition Plant (CAAP)

RDX, TNT, 2,4- and 2,6-DNT, 1,3,5-TNB, and nitrobenzene (NB) have been detected in a groundwater plume emanating from the CAAP near Grand Island, Nebraska. Wartime operations between 1942 and 1973 produced an *estimated* total waste discharge of 26,410 kg of TNT (WWII, Korean, and Vietnam conflicts) and 7,300 kg of RDX (Korean) (Doesburg and Bond 1984). Contamination is observed at 64 sites, including wastewater pond, burn pits, and leaching pits. The CAAP was an explosives production and munitions packing facility.

The affected primary aquifer is an unconfined, "relatively homogeneous," fluvial, sandy gravel, deposited by late Quaternary streams flowing from the west and northwest. The aquifer facies includes some small-scale, "sporadic, laterally discontinuous, sand and silt lenses" originating from irregular paleo-channel formation. The primary aquifer is approximately 18 m thick, with a transmissivity coefficient from 0.0072 to over 0.01 $m^2 \cdot s^{-1}$ (Keech and Dreeszen 1964). The aquifer material is likely to be low in organic carbon (potential sorption or reaction substrate).

Well level data from November 1984 indicated a northeastward ground-water flow in the sand and gravel aquifer at a very high rate of approximately 175 $m \cdot yr^{-1}$ (0.48 $m \cdot d^{-1}$, unpublished data of Cady and Spalding as cited in Spalding and Fulton (1988)). This longitudinal velocity is consistent with estimates based on the RDX plume position relative to production (release) time.

Spalding and Fulton (1988) delineate the contaminant plumes in three dimensions in order to ascertain the relation between CAAP operations and off-facility nitrate contamination. The RDX transport is described as largely conservative and flow dependent. RDX sorption onto sandy aquifer material is low; the dimensionless $K_{d,sand}$ = 1.6 (Tsai, Davis, and Benioff 1985). The K_d concept is described in Chapter 5. Aerobic transformation of RDX is considered negligible (McCormick, Cornell, and Kaplan 1978). No evidence of anaerobic degradation such as hydrazine metabolites (McCormick, Cornell, and Kaplan 1978) is observed at CAAP. Variations in RDX concentrations

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along the 6.5 km long, classically cigar-shaped plume are attributed to variations in source strength, which may be attributed to production schedule as well as residence time in wastewater lagoons where RDX would be subject to photolytic breakdown (Spanggord et al. 1980a,b; McCormick, Cornell, and Kaplan 1981). The RDX plume also plunges at about 0.5 m·yr^{-1} due to surface recharge.

The TNT and nitrate distributions indicate nonconservative behavior. Despite an estimated four-fold greater production of TNT (versus RDX) over a longer time period, the off-facility, TNT plume is only 0.8 km long and ≤ 0.1 km wide. Spalding and Fulton (1988) attribute the lesser TNT dispersal to possible photodegradation in wastewater ponds, aerobic biotransformation, and/or stronger sorption to aquifer sands (dimensionless $K_{d,\ sand}$ = 53 $\pm$ 20 (Spanggord et al. 1980a,b)). Unfortunately, dissolved oxygen, EH, or other corroborating evidence of biotransformation apparently has not been collected at the CAAP site. Spalding and Fulton (1988) attribute the nitrate source to local agricultural activity and speculate that nitrate disappearance is due to nitrate reduction.

The key observations to carry forward from these very brief overviews of XAC transport are as follows:

a. TNT transport is much more retarded than RDX, even in a highly permeable, sandy aquifer with little organic carbon.

b. Advective transport, which depends on aquifer permeability, is the underlying control of XAC transport.

c. Sorption and reaction processes may retard XAC transport severely.

d. Most remedial investigation studies do not begin to approach the level of complexity needed to understand subsurface XAC transport.

2.4 Subsurface Media Concepts

The physical and chemical nature of subsurface media is a fundamental influence on contaminant transport, as suggested by observations at the LAAP and CAAP sites. Any numerical modeling effort requires a conceptualization of the subsurface media because that conceptualization drives the selection of flow equations. Likewise, the conceptualization of the predominant biogeochemical processes drives the selection of an appropriate suite of reaction and transport equations. Process descriptors entail multiple assumptions (explicit or implicit), including some concerning the transport medium, as will be demonstrated in later chapters.

All subsurface media are heterogeneous. These heterogeneities include spatial and/or temporal variations in mineralogy, porosity, permeability, microbial populations, and solutes. Each of these variables can have

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significant impact on the fate and transport of XACs. The subject of hetero-geneity is a recurring theme in this report because explosives are susceptible to multiple, simultaneous reactions involving multiple components and structures in the subsurface media. This aspect of the subsurface has been minimized (in many cases erroneously) in existing numerical models, primarily due to the lack of (1) a quantitative understanding of the influence of heterogeneities on solute transport, (2) methods to relate processes or properties to the scale of numerical discritization, i.e., the scaling problem, and (3) the absence of techniques to quantify the heterogeneities. Very few process descriptors explicitly attempt to incorporate the influence of subsurface heterogeneities on solute transport, and practical application of these is impeded by the scarcity of appropriate field characterization. Evaluating and modeling the impact of heterogeneities on transport and remediation processes is an active area of current research.

The present discussion focuses on porous media rather than fractured or fractured porous media. Porous media are the most common near-surface media (e.g., soils) and are therefore the most immediately impacted by anthropogenic contaminants. Flow and transport through porous media are relatively better understood, at least for homogeneous media, and therefore are conceptually and numerically less difficult to model. Saturated and unsaturated flow concepts are introduced. Structured and fractured media are discussed briefly.

Porous media concepts

Characterization of porous media requires definition of several fundamental properties common to many process descriptors. The level of characterization depends on the processes of interest and scale of investigation. For process modeling at the bench scale, one may require estimates of the bulk porosity, pore size variation (intraparticle and interparticle), surface area, mineralogy, etc. At the field scale an averaged (scaled or effective) value of porosity, permeability, dispersivity, and perhaps storativity may be all that is required for a given model.

The total porosity (n_T) is the ratio of total void volume $(V_V$, i.e., not occupied by solids) to the bulk volume (V_b) of a representative block of the medium. Not all of the pore space in the block may be readily accessible to fluids moving through it; some pores such as intragranular voids may be completely isolated. The effective porosity (n_e) is the porosity readily accessible to flowing water, which is typically less than n_T. Porosity tends to vary directly with sorting (homogeneity in particle sizes) and inversely with age because of desiccation, compaction, and cementation (precipitation of minerals within pore spaces).

Water saturation (S_w) is the proportion of porosity occupied by water, ranging between 1 (fully saturated) and zero (dry). The pore space not

occupied by water is occupied by air, so air saturation, S_a, equals $(1-S_w)$[1]. When S_w is less than 1.0, the medium is unsaturated or partially saturated. Unsaturated conditions predominate in the porous medium between the land surface and water table, the surface defined by points where pressure within the aqueous phase is atmospheric. Above the water table is the vadose zone in which pressure in the water phase may be less than atmospheric (negative gage pressure) due to capillary tension drawing water into small pores (assuming the soil particle surfaces are hydrophilic). Pore pressure below the water table generally increases hydrostatically.

Flow and transport under unsaturated conditions are complicated by the mutual impedance to flow of the air and water phases. Since capillary pressure increases nonlinearly as water saturation decreases, the constitutive relations between permeability, saturation, and pressure are nonlinear. Rarely does S_w reach zero.

Numerical modeling of groundwater flow requires that the porous media be discritized into blocks or elements of sufficiently uniform properties that an averaged parameter value adequately represents that block. Averaged values vary with the volume scale of observation, becoming more or less stable at the representative elementary volume (REV) (see Freeze and Cherry (1979) or any introductory text on groundwater). Some form of volume averaging is unavoidable in numerical modeling of groundwater flow and transport. Determining the optimal averaging (or scaling) procedure for various processes is currently an active area of investigation.

Depositional environment and heterogeneities

Several process descriptors, particularly some of those dealing with advection, dispersion, diffusion, and sorption, try to capture the influence of physical and chemical heterogeneities in porous media. It is becoming increasingly apparent that refined topological definition of lithologies and characterization of their heterogeneities are required for more accurate prediction of flow and contaminant transport (Anderson 1992, Molz et al. 1990).

Physical heterogeneities in porous media are primarily the product of spatial and temporal variations in the sediment supply and carrying capacity of the flow systems from which the sediments were deposited, i.e. their depositional environment (e.g., fluvial, lacustrine, glacial, aeolian). Depositional processes tend to sort out particles by grain size. Since there is at least a weak correlation between mineralogy and grain size, geochemical heterogeneities tend to mimic lithologic patterns. For example, strong fluvial currents tend to keep fine-grained clay and organic particles in suspension while sands and gravels are depositing. The fine-grained suspended materials settle in lower energy environments such as floodplains or lakes.

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[1] Nonaqueous phase liquids, NAPLs, are not considered here.

Post-depositional changes, such as desiccation, soil genesis, cementation, and compaction, also may superimpose new heterogeneities and physical structures. Soil zones tend to be highly active biologically, hosting bacteria, rooted macrophytes, insects and other burrowing animals. The high organic content of many soils may increase the retention of organic contaminants, including explosives. However, bioturbation and/or desiccation can create macropores through which XAC leachate may flow preferentially and thereby accelerate contaminant transport toward the saturated zone.

Several process descriptors quantitate diffusive, mass exchange between high permeability regions and low permeability regions. The low permeability regions occur at multiple scales. At the pore scale, diffusive exchange may occur within intraparticle pores, microfractures, or clay mineral interlaminae. At a larger scale, diffusive processes involving soil aggregates, structured soils, or lithic fragments may be significant. Finally, at the field scale, diffusive exchange with fine-grained lithofacies may be a rate limiting process on pump-and-treat "remediation."

Grouping or classifying sediment types based on lithology defines lithofacies, e.g. a sandy facies or fine-grained facies. The term facies is derived from a Latin word referring to the external appearance of something (Walker 1984). Subsurface media can be classified by any number of properties. In hydrogeology, permeability is one of the most important properties, thus media can be lumped according to their hydraulic properties into hydrofacies. Lithofacies and hydrofacies are often the same but are not necessarily so.

Fractured or cavernous media

Fractured media are characterized by the presence of discrete cracks along which water and contaminants may flow preferentially. Contaminant transport in fractured systems is of great concern because fractures may act as high velocity conduits for dispersal. Numerical modeling of transport in fractured media can be quite challenging for these reasons:

a. Delineation of fracture orientation, extent, and connectivity is very difficult, requiring field observation (e.g., pump and tracer tests), lineament analysis (remote sensing), and/or borehole visualization.

b. Aperture dimensions, required in many numerical models for discrete fracture flow, is difficult to ascertain.

c. Flow may be high enough to become turbulent or non-Darcian, requiring special treatment.

d. Mass transfer between fractures the inter-fracture matrix, typically characterized by lower flow velocities, may be significant, particularly in fractured porous media.

Crystalline igneous or metamorphic rock and consolidated sedimentary rock (e.g., limestone, sandstone) are likely to be fractured, particularly if it has been subject to significant compaction or tectonic forces, such as mountainous terrane. Basaltic rocks (volcanic) typically fracture upon cooling and may also contain lava tubes (tunnels through which lava had flowed). In carbonate terranes flow along fractures can cause preferential dissolution, which increases the aperture (distance between the two walls of the crack); the extreme case of this process would be the formation of caves.

Fractured media near the surface are common in the United States:

a. In north-central U.S. and Canada (glaciated, Precambrian shield areas).

b. In volcanic terranes underlain by basalt (e.g., extensive regions of Hawaii, Idaho).

c. Carbonate terrane where karst features may develop (e.g., Florida, Indiana, and many other areas). Fractured media may be present under thin veneers of glacial sediments, presenting an additional challenge to both remediation and remediation modeling.

3   Advective-Dispersive Transport

Advective-dispersive transport (**ADT**) is the underlying process governing the subsurface migration of contaminants. All other active, environmental processes of interest here require the physical movement of solutes (reactants and reaction products). Transport and remediation modeling begins with an ADT equation and adds other process terms as needed. Of course, some of these processes can be so active that they become as important as ADT, particularly when advection is slow. Under certain conditions, some explosive associated compounds (XACs) are susceptible to rapid transformation reactions, precluding extensive transport of the reactant XAC; however, the reaction product(s) may not be so labile and ADT increases in relative importance.

Advective transport refers to the passive movement of a solute with flowing water (or other solvent). Advective transport in the vapor phase may be of marginal significance for a few small molecular weight XACs or reactants involved in their transformation (see Chapter 6). Advection in nonaqueous phase liquids (NAPLs) is not directly relevant to explosives transport and is not reviewed here.

Dispersion is the general term applied to the observed spreading of a solute plume and is generally attributed to hydrodynamic dispersion and molecular diffusion. Hydrodynamic dispersion is a physical process in which macroscopic spreading arises from the multiple variations in flow path velocity and tortuosity. Molecular diffusion is a physicochemical process resulting from the Brownian motion of molecules, resulting in a net migration down a chemical gradient.

The following discussion focuses on aqueous phase flow and transport in porous media, primarily soils and unconsolidated, sedimentary aquifers. Flow and advection are reviewed in Section 3.1. Diffusion process descriptors and parameter estimation methods are discussed in Section 3.2. Advection-dispersion equations for porous, structured, and fractured, saturated media are reviewed in Section 3.3. Flow and transport in unsaturated media are sufficiently unique and important to be treated separately (Section 3.4). Recommendations for research related to XAC advective-dispersive transport are

offered in Section 3.5. Many of the descriptors here will apply to vapor phase ADT discussed in Section 6.3.

3.1 Flow and Advection

Flow in porous media is generally described by some form of Darcy's equation. For single-phase flow of an incompressible fluid in an isotropic medium, the one-dimensional Darcy equation is:

$$q_i = \frac{Q_i}{A_{j,k}} = -K_i \frac{\partial h}{\partial l_i} \qquad (3\text{-}1)$$

where specific discharge, q_i [L·T^{-1}], is defined as the volumetric discharge, Q [L^3·T^{-1}], through a unit, cross-sectional area, $A_{j,k}$ [L^2], normal to flow direction i (orthogonal to coordinates j and k). Darcy's equation is an empirical description of the dependence of q_i on hydraulic conductivity, K_i [L·T^{-1}], and the head gradient, $\partial h/\partial l_i$.

The hydraulic conductivity depends on both the intrinsic permeability (k_i [L^2]) of the medium and the density (ρ_α [M·L^{-3}]) and dynamic viscosity (μ_α, M·L^{-1}·T^{-1}) of fluid α: $K = k_i \rho_\alpha g/\mu_\alpha$. The water equivalent head, or simply head, h [L], in Equation 3-1 is a convenient surrogate for the potential energy, the sum of the elevation, z [L], above an arbitrary datum and the local pressure head, $P/(\rho_\alpha g)$ [L]: $h = z + P/(\rho_\alpha g)$, where P is the gage pressure [M·L^{-1}·T^{-2}], ρ_α is the density of phase α [M·L^{-3}], and g is acceleration due to gravity [L·T^{-2}]. Substituting the preceding definitions for K and h into Equation 3-1 yields:

$$q_i = -\frac{k_i \rho_\alpha g}{\mu_\alpha} \frac{\partial}{\partial x} \left[z + \frac{P}{\rho_\alpha g} \right] \qquad (3\text{-}2)$$

A head gradient may result from an imposed pressure gradient, $\partial P/\partial x$ (injection into a confined aquifer), and/or a potential energy gradient ($\partial z/\partial x$) due to elevation difference (Δz) across Δx along the flow length l_i. The energy term in the parentheses neglects the contribution of flow velocity, which typically is assumed to be negligible in porous media.

Hydraulic conductivity will be referred to subsequently as simply conductivity unless otherwise indicated; likewise, permeability may be taken as equivalent to intrinsic permeability. Cartesian coordinates are adopted throughout this report, with the primary horizontal flow along the x coordinate, z as the vertical (positive downward), and y normal to the x-z plane. Radial flow and transport are not discussed in this review.

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Implicit in the Darcy equation (Equations 3-1 and 3-2) are several assumptions about the fluid and porous medium. Darcy's equation assumes that the influence of fluid flow velocity on head is negligible (recall $V^2/2g$ of the Bernoulli energy equation). The Reynolds number (Re) for porous media defined as

$$Re = \frac{q\,d}{\nu} \qquad or \qquad = \frac{q\sqrt{k}}{\nu} \qquad (3\text{-}3)$$

is a dimensionless parameter relating inertial to viscous forces, where q is specific discharge [$L \cdot T^{-1}$], ν is kinematic viscosity [$L^2 \cdot T^{-1}$], and d is a characteristic length of the medium (de Marsily 1986). In pipe flow the d is the wetted perimeter; there is no general agreement as to an analogous length in porous media, though the average particle diameter or the effective diameter (e.g. d_{10}, the diameter larger than only 10 percent by weight of the particles) is used commonly. Darcy's equation is generally considered applicable for flow conditions with a porous medium Re not in excess of a critical threshold between 1 and 10 (Bear and Verruijt 1987). At high velocities, the inertial forces become significant relative to viscous drag against media walls and intra-fluid friction. In fine-grained media the high wetted surface area and low velocities may result from water-media interactions resulting in non-Darcian flow.

To summarize, the Darcy equation (Equation 3-1) assumes:

- Flow is approximately laminar and inertial forces are negligible.

- Fluid and solid phases are incompressible.

- Fluid viscosity and density are constant.

Extensions to heterogeneous media and multiphase flow are common; the validity of this extension is an assumption. Under natural gradient conditions, most groundwater flow velocities are usually sufficiently low for laminar to predominate. Only in large fractures (e.g., karst, fractures) or close to pumping wells may flow become fast and depart from the linear Darcy equation (Bear and Verruijt 1987). The incompressibility assumption is reasonable at the bench scale but tenuous at the field scale. Variation in liquid viscosity and density is small as long as solute concentrations and temperatures remain reasonably uniform. Very small density differences can induce unstable flow (e.g., stratified flow).

Fluid phases in the subsurface flow in response to hydraulic pressure gradients as indicated in Equation 3-2. Natural or imposed gradients may be the result of spatial variations in groundwater recharge or discharge. Aquifer recharge may occur via injection wells, precipitation infiltration, leakage from surface water bodies, or interlayer flow (e.g., leaky aquitards). Discharge

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may be via withdrawal or recovery wells, evapotranspiration, or seepage out of the aquifer to the surface (springs) or other aquifers. These stresses and their effects on groundwater flow must be known or approximated in order to anticipate contaminant migration pathways for risk analysis, plume control, and aquifer remediation.

Specific discharge units of (volume/time)/area reduce to velocity units $L \cdot T^{-1}$; thus, q is often referred to as "Darcy velocity" or filtration velocity. To avoid confusion with other velocity terms related to the Darcy equation, the term specific discharge is preferable to Darcy velocity. A more meaningful velocity term is seepage velocity (v), which incorporates the influence of the reduced, effective area through which flow actually occurs in porous media by dividing q by the dimensionless, effective porosity n_e. Seepage velocity may be conceptualized as the average velocity of a miscible displacement front through a porous medium. Since terminology is by no means universal, readers must be wary of any author's definitions. All subsequent use of the term velocity will refer to seepage velocity.

Anisotropy of permeability is the rule in groundwater; i.e., permeability (k) or conductivity (K) varies with the direction of flow. This anisotropy is intuitively obvious when considering, for example, flow through a sandy aquifer with intercalated silt and clay layers—the permeability parallel to the bedding plane is much greater than normal to it. It may be helpful to conceptualize the directional variation of the permeability tensor values as a flattened ellipsoid, the minor axis of which is normal to bedding. Permeability values in natural media tend to show a log-normal distribution and may show directional contrasts of over 10 orders of magnitude (Freeze and Cherry 1979).

A frame of reference must be adopted for numerical modeling; typically, Cartesian coordinates (x, y, z) with the primary flow direction along one of the reference axes. Only three components of flow velocity vector need be considered with this convention. The next simplifying assumption is that $k_x = k_y \neq k_z$, or that permeability parallel to bedding is homogeneous (laterally isotropic). Numerous analytical and simple numerical models assume permeability isotropy ($k = k_x = k_y = k_z$) for the sake of computational ease. Though this assumption is never strictly valid, useful preliminary calculations often can be made utilizing the concept.

Solute transport models require an expression for mass balance or conservation. For the one-dimensional, advective transport of a single constituent, the mass balance equation may be described as:

$$\frac{\partial C_i}{\partial t} = -\frac{\partial C_i v_x}{\partial x} \tag{3-4}$$

where v_x is the seepage velocity ($= q_x / n_e$). If v_x does not vary along X (i.e., n_e is spatially uniform), Equation 3-4 becomes

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$$\frac{\partial C_i}{\partial t} = -v_x \frac{\partial C_i}{\partial x} \qquad\qquad (3\text{-}5)$$

where C_i is the concentration of solute i.

3.2 Dispersion and Diffusion

Dispersion is a general term applied to the observed spreading and dilution of a solute plume as it passes through a subsurface medium. Classical hydrodynamic dispersion is due to spatial variations in advective transport at multiple scales (pore scale to field scale). The random motion of solute molecules drives molecular diffusion of the solute in the direction of lower concentration (down the chemical gradient). Descriptors and parameter estimation equations are presented below.

Molecular diffusion

Molecular diffusion is the net migration of solute molecules from regions of higher concentration to regions of lower concentration. This migration is due to the random motion of solute molecules. Traditionally, this process has been considered negligible relative to hydrodynamic dispersive effects, or at least unresolvable from it, and is usually lumped into a dispersion coefficient. The presumption that molecular diffusion is relatively insignificant appears to be valid for certain advection-dominated systems. However, there is a growing appreciation for the solute-retarding effects of molecular diffusion.

· Diffusive mass transport can play a significant role at several scales, and is an integral part of several process descriptors reviewed in this report (Table 3.1 lists several specific examples). The relative significance of diffusion appears to depend on the scale (time and space) of observation. While intraparticle and intra aggregate diffusion may be an important cause of nonequilibrium partitioning (see Chapter 5) in bench-scale experiments, they may be insignificant relative to diffusion into fine-grained strata at the field scale. The time frame of the larger scale, field phenomena tends to be much greater than for intraparticle diffusion, largely because of the much shorter travel times of the latter (Goltz and Roberts 1988). Diffusion limited controls have been invoked to account for the nonequilibrium processes and hysteretic effects on sorption (e.g., Ball, Curtis, and Roberts 1992).

One-dimensional, diffusive, mass flux, F [$M{\cdot}L^{-2}{\cdot}T^{-1}$], through a unit cross section of isotropic media is directly proportional to the concentration gradient and is typically described using Fick's first law (Crank 1975):

Table 3.1
Summary of Processes in Which Diffusive Transport is Important

Nonequilibrium Diffusion Processes	Boundary Layer Diffusion Processes
Intragranular or intraparticle diffusion	Sorption kinetics
Intra-organic matter diffusion	Biofilm kinetics
Intra-aggregate diffusion	Volatilization
Intralayer (bed, stratum) diffusion	
Fracture-matrix or macropore-matrix diffusion	

$$F = - D_x \frac{\partial C}{\partial x} \qquad (3\text{-}6)$$

where D_x $[L^2 \cdot T^{-1}]$ is the dispersion coefficient (or diffusivity) in the x-direction. The gradient, $\partial C / \partial x$, is negative in the direction of mass transport by convention (Freeze and Cherry 1979). Fick's second law describes the temporal variation of concentration along x due to diffusion:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial_x} \left[D_x \frac{\partial C}{\partial x} \right] \qquad (a)$$

$$= D_x \left[\frac{\partial^2 C}{\partial x^2} \right] \qquad (b) \qquad (3\text{-}7)$$

for media with spatially variable (3-7a) and homogeneous (3-7b) diffusivities.

Many methods have been developed to predict molecular diffusivities for solutes in water, air, and other solvents. The diffusion coefficients at infinite aqueous dilution may be estimated as follows (de Marsily 1986, p 232):

$$D_w = \frac{RT}{N} \frac{1}{6 \pi \mu r} \qquad (3\text{-}8)$$

where R is the gas constant [$M \cdot L^2 \cdot T^{-2} \cdot K^{-1} \cdot mol^{-1}$; e.g., 8.3144 $J \cdot K^{-1} \cdot mol^{-1}$], T is temperature (°K; = °C + 273.15), N is Avogadro's number [6.023×10^{23} atoms/mole], μ is the viscosity [$M \cdot L^{-1} \cdot T^{-1}$], π is pi [dimensionless; ≈ 3.1459], and r is the mean radius [L] for the diffusing molecular aggregate, including any associated water molecules.

Tucker and Nelken (1990) and Reid, Prausnitz, and Polin (1987) recommend the method of Hayduk and Laudie (1974) for estimating diffusivities or organic solutes (infinite dilution) in water:

$$D_w = \frac{13.26 \times 10^{-5}}{\mu_w^{1.14} \; V'^{0.589}_B}$$

(3-9)

where μ_w is the dynamic viscosity of water at the desired temperature $[M \cdot L^{-1} \cdot T^{-1}]$, and V'_B is the molar volume of the solute which can be estimated by the LeBass method (see Tucker and Nelken 1990).

Diffusion coefficients for explosives contaminants in water at 25 °C are estimated to be on the order of 6-10 $\times$ 10^{-6} cm$^2 \cdot$s^{-1} (Rosenblatt et al. 1989), compared to 5-20 x 10^{-6} cm$^2 \cdot$s^{-1} for water and common environmental ions (H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^-, SO_4^{2-}). Table 3.2 lists measured or estimated molecular diffusion coefficients for several XACs in water and air. Diffusion coefficients are generally directly proportional to temperature, but appear independent of ionic strength (Freeze and Cherry 1979). Methods to estimate solute dispersivity in air are discussed in relation to volatilization (Chapter 6).

Molecular diffusion within a porous medium is impeded by the tortuous path imposed by the impervious solids. An effective diffusivity (D_e) is defined to describe this obstructed diffusion by introducing an empirical, tortuosity coefficient, ω (dimensionless):

$$D_e = \omega \; D_w$$

(3-10)

The ω is commonly 0.5 to 0.01 for laboratory experiments on common aquifer media (Freeze and Cherry 1979). Many equations have been proposed to estimate the tortuosity coefficient, for example: $\omega = n_e^{4/3}$. Of course, sorption and other reactions in porous media may retard the diffusive transport of organic solutes.

Hydrodynamic dispersion and macrodispersion

Classical hydrodynamic dispersion is the observed spreading of a solute plume due to mechanical or advective processes. Flow or seepage velocities vary spatially over a wide range of scales. The flow velocity profile across a pore, by analogy to pipe flow, would have a no-slip boundary (v = 0) at the wall due to viscous drag, and the fastest flow at the pore center. Solute dispersion induced by this relatively simple, pore-scale flow variation is enhanced in porous media by the irregular undulations in pore diameter (pores

Table 3.2
Summary of Molecular Diffusion Coefficients in Air and Aqueous Phases for Common Explosives, Associated Contaminants, Homologous Compounds, and Representative Common Organic Contaminants[1]

Compound	Vapor Diffusion Coeff., $D_{X/A}$ (cm^{2}sec^{-1})	Aqueous Diffusion Coeff., $D_{X/W}$ x 10^{-6} (cm^{2}sec^{-1})
Explosives and Associated or Homologous Aromatic Contaminants		
RDX[2]	0.074	7.15
HMX[2]	0.063	6.02
Tetryl[2]	0.059	5.99
TNT[2]	0.064	6.71
Dinitrotoluene[2] (all isomers)	0.067	7.31
Nitrotoluene	0.070[3]	8.10[4]
Toluene	0.088[5] (30)	9.10[4]
Trinitrobenzene[2]	0.068	7.20
Dinitrobenzene[2]	0.073	7.94
Nitrobenzene	0.080[3]	8.85 [4]
Benzene	0.088[5]	10.3[4]
Aniline (amino-benzene)	0.072[5]	9.5[4]
Toluidine (amino-toluene)	0.076[3]	8.52[4]
Non-Aromatics		
Water	0.256[5]	31.0[4]
Oxygen	0.206[5]	23.5[5], 31.0[4]
Carbon Dioxide	0.164[5]	17.7 (20° C)[5] 20.6[4]
Ammonia	0.28[5]	24.8[4]
Trichloroethene	0.083[3]	9.65[4]

[1] Temperature is 25 °C, unless otherwise noted.
[2] Rosenblatt et al. (1989); vapor coefficients estimated by Fuller-Schettler-Giddings (FSG) method and aqueous coefficients predicted by Hayduk-Laudie (HL) method (Tucker and Nelken 1990).
[3] Estimated by FSG method.
[4] Estimated by HL method; HL does not distinguish isomers (Tucker and Nelken 1990).
[5] Thibodeaux (1979).

versus pore throats) and the tortuous paths resulting from the random and varied divergences and convergences of flow. At a larger scale, permeability variations arise from geologic fabric (heterogeneities) which further divert and disperse solute advection. As the volume of medium traversed by a parcel of solute-bearing water increases, the chance of encountering media of contrasting permeability also increases, causing an increase in apparent dispersion (or macrodispersion). Mechanical dispersion as described here is also referred to as kinetic dispersion (de Marsily 1986). Morel-Seytoux and Nachabe (1992)

suggest that dispersion may also be caused by heterogeneous boundary conditions.

The scale dependence of dispersion has been the subject of considerable research over the last decade (see macrodispersion discussion below). Although there is now a general consensus that this scale dependence is due to spatial variations in permeability, there is no agreement as to the most effective way to predict dispersion for transport modeling purposes. Other transport processes may be susceptible to spatial variations in media properties.

Dispersion of a contaminant plume is a three-dimensional process. Dispersion along the predominant flow direction, longitudinal dispersion, is typically much greater than the transverse dispersion lateral to the main flow direction. In sedimentary aquifers vertical dispersion is typically the smallest due to constraints imposed by large, vertical variations in permeability. For one-dimensional transport, such as in column experiments or many vadose zone models, only longitudinal dispersion is relevant.

In packed column experiments, the observed tailing of breakthrough curves (BTC; $C_{effluent}$ versus time) can be attributed largely to these virtually infinite number of available transport pathways. Imagine, for example, a slug of solute-bearing water entering a packed column (C_{in} = 1.0 for x = 0, over some short Δt), initially containing clean interstitial waters (C = 0 at x > 0, t = 0). Even in "homogeneous" media some parcels of solute-bearing water will travel along relatively high velocity and/or low tortuosity pathways; these parcels move ahead of the advancing solute front (defined as the median concentration, C = 0.5 C_o) and mix with ambient waters. Likewise, other parcels will travel along relatively low velocity and/or high tortuosity paths and lag behind the slug front. In one-dimensional, miscible displacement experiments, this mechanical dispersion manifests itself as the early and delayed "tails" in the solute BTC, ideally symmetrical about the median concentration.

The dispersion coefficient in Equation (3-7) effectively represents the sum of hydrodynamic dispersion and molecular diffusion. For two-dimensional (areal) transport, the longitudinal (D_L ; $L^2 \cdot T^{-1}$) and transverse (D_T) dispersion coefficients may be defined as:

$$D_L = \alpha_L v + D_{Eff} \qquad (a)$$
$$D_T = \alpha_T v + D_{Eff} \qquad (b) \qquad\qquad (3\text{-}11)$$

where α_L and α_T are, respectively, the longitudinal and transverse dispersivities [L], empirical coefficients describing the dependence of dispersion on seepage velocity (v) in the primary flow direction. Bench-scale dispersivities for homogeneous media range between 0.01 and 10.0 cm, whereas field scale measures are much higher, on the order of 10 cm to over 100 m in highly heterogeneous, porous media (Anderson 1984). Transverse dispersivity is typically a small fraction (0.01 to 0.20) of the longitudinal dispersivity

(de Marsily 1986). In sedimentary aquifers, vertical dispersivities are generally $\leq 0.1 \ \alpha_L$, while lateral transverse dispersivities are on the order of 0.1 to 0.3 α_L. The actual dispersivity ratios are highly site specific. These ratio ranges are intended only to convey relative magnitudes; any a prior application to a field site should be as a preliminary, first estimate in the absence of field measurement or model calibration.

Mechanical dispersion and molecular diffusion are difficult to resolve at any scale of observation, and therefore their effects usually are lumped into single-dispersion coefficients. In practice, these parameters are obtained by fitting (calibrating) some form of the ADT equation to observations. Kirda, Nielson, and Biggar (1973) suggest that diffusion in soils becomes relatively insignificant as seepage velocities exceed approximately 0.002 cm·s^{-1} (1.7 m·d^{-1} or 631 m·yr^{-1}). This velocity is fairly high, suggesting that diffusion is significant ($\geq$ 1 percent difference) under many groundwater flow conditions.

The dispersion coefficient can be estimated based on an analysis of pulse tracer discharge data by:

$$D_L = \frac{\sigma_L^2}{2 \, t} \tag{3-12}$$

where σ_L^2 is the spatial variance in concentration and t is the travel time (Dominico and Schwartz 1990). A normal distribution of the plume slug is assumed. Note also that the influence of diffusion is not explicitly considered. Transverse dispersion would be likewise defined and the variance based on lateral spreading. If velocity is constant, v/x can be substituted for $1/t$ in Equation (3-12), where x is the travel distance from the source to the plume center.

The dispersion equation above (Equation 3-12) is based on spatial variation in concentration. In column breakthrough experiments, the variation of the effluent concentration over time is measured. Robbins (1983) defines the longitudinal dispersion coefficient in terms of temporal variance in concentration (σ_t):

$$\sigma_L^2 = v^2 \, \sigma_t^2 \tag{3-13}$$

and thus,

$$D_L = \frac{v^2 \, \sigma_L^2}{2\,t} \qquad\qquad (3\text{-}14)$$

The standard deviation, σ_t, (σ^2 = variance) may be estimated graphically from the breakthrough curve as the average of the arrival times of concentrations (C) of 0.16 C_o and 0.84 C_o, where C_o is the constant inflow concentration, i.e., $\sigma_t = 0.5 \, (t_{84} - t_{16})$ (Dominico and Schwartz 1990). Other approaches for estimating D_L from BTC's are available (e.g., Levenspiel 1972).

Macrodispersion in heterogeneous media

As indicated in the general advection-dispersion equation (3-2), dispersion is modeled traditionally as a Fickian process. Strictly speaking, adopting a Fickian model assumes that the plume attains a gaussian (normal) distribution. Field tracer studies indicate that a normal distribution is approached only after some significant travel distance from a point source. Over short distances from a point source, concentration versus time trends tend to show an early breakthrough. Estimates of this minimal mixing distance range from 10's to 100's of meters (Anderson 1984, Gelhar et al. 1985). Numerical experiments by Smith and Schwartz (1980) suggest that a normal distribution in heterogeneous media may never be attained. These arguments suggest that the Fickian model may be inappropriate for typically small-scale remediation efforts.

The scale dependence of dispersion is well established. Analysis of a large set of field data indicates that the dispersion coefficient increases roughly asymptotically with distance from the source (Anderson 1984, Gelhar et al. 1985, Molz et al. 1990). Macrodispersion is the term applied to field scale, hydrodynamic dispersion, largely dominated by the permeability heterogeneities of the medium (Schwartz 1977, Molz et al. 1990). As the plume spreads, it encounters different lithologies which impact the cumulative dispersion. Nonspecific field sampling techniques (e.g., samples from open wells or those with long, screened intervals) increase the apparent dispersion by diluting the sample at the well. New techniques to more precisely delineate variation in conductivity (see Molz et al. 1990) indicate that with higher resolution measurements (e.g., from the contaminated interval only), smaller and more meaningful, less scale-dependent, dispersion parameters are obtained.

The traditional ADT equation does not capture the scale-dependence of dispersion. Several attempts have been made to quantitate the scale dependence. For example, Gelhar and Axness (1983) developed expressions for longitudinal (A_L^*) and transverse (A_T^*), asymptotic macrodispersivities based on geostatistical evaluation of hydraulic conductivities [as ln(K)]:

$$A_L^* = A_L + \alpha_L + \frac{D_e^*}{v} \qquad (a)$$

$$A_T^* = \alpha_T + \frac{D_e^*}{v} \qquad (b)$$

(3-15)

where A_L is the longitudinal asymptotic dispersivity defined as

$$A_L = \frac{\sigma_Y^2 \lambda}{\gamma_2}$$

(3-16)

and σ_Y^2 is the variance of the ln(K) data (Y = ln(K)), λ is the correlation length scale, and γ is a flow factor (≈ 1). Setting the transverse asymptotic dispersivity to zero suggests that bedding heterogeneities preclude transverse macrodispersivity. Equations 3-15a and 3-15b include effects of macroscopic mechanical dispersion due to heterogeneities (A_L), pore-scale mechanical dispersion (α terms), and effective diffusion. Most of the longitudinal macrodispersion is attributable to the A_L term of Equation 3-15a, the other two terms being relatively small (Dominico and Schwartz 1990). The drawback to such geostatistical approaches is that a considerable amount of high resolution conductivity data are required. In situ borehole flowmeters, which measure vertical variations in horizontal conductivity, hold promise in this regard (Molz et al. 1990).

3.3 Advection—Dispersion Descriptors

The advective-dispersive transport formulation with dispersion modeled as a Fickian process is by far the most widely used framework upon which additional process formulations are developed. The limitations of the ADT model are offset by its simplicity and ease of use. The traditional ADT expression works reasonably well when applied to small-scale (~ 1 m), laboratory experiments with homogeneous media. Thus, ADT models will remain useful for process research.

One of the most frustrating aspects in the field application of traditional ADT-based numerical models (as Equation 3-17) is that permeability and biogeochemical heterogeneities occur at scales much smaller than is practical to tessellate for the numerical grid. As has been mentioned previously, the heterogeneous flow and transport fields are the cause of the scale-dependency of fitted model parameters. Several attempts have been made to capture the salient features of natural heterogeneities and describe their effects on solute transport. Some of these concepts are introduced below and in conjunction with the discussion of physical nonequilibrium sorption (Chapter 5).

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Porous media

A simple mass balance expression for the one-dimensional, transient transport of a single constituent, incorporating advection, dispersion, and general terms for sources, sinks, and biogeochemical reactions is (Anderson 1984):

$$\underbrace{\frac{\partial C_i}{\partial t}}_{\substack{\text{Change in}\\ \text{mass storage}}} = \underbrace{-\frac{\partial C_i v_x}{\partial x}}_{\text{Advection}} + \underbrace{\frac{\partial}{\partial x}\left[D_x \frac{\partial C}{\partial x} \right]}_{\text{Dispersion}} + \underbrace{\frac{C_W W}{n_e}}_{\substack{\text{Source}\\ \text{or Sink}}} + \underbrace{\sum_{k=1}^{K} R_k}_{\text{Reactions}} \qquad (3\text{-}17)$$

where C_i is the concentration of solute i [$M \cdot L^{-3}$], t is time [T], V_x is seepage velocity in the x direction [$L \cdot T^{-1}$], and D_x is the dispersion coefficient [$L^2 \cdot T^{-1}$]. The volumetric flow rate per unit volume of aquifer (W; T^{-1} [$L^3 \cdot T^{-1}/L^3$]) with solute concentration C_W [$M \cdot L^{-3}$] may be a source (+; e.g., recharge, injection) or sink (−; e.g., discharge, withdrawal). All biogeochemical processes are represented by the K reactions terms described by ΣR_k. These reactions represent sources and sinks and are discussed in Chapters 4 through 8 of this report.

The transport equation is typically decoupled from the flow Equations 3-1 and 3-2, i.e., these sets of equations may be solved separately in an alternating fashion. The decoupling is valid as long as changes in the solute concentration (or other model variables such as biomass) resulting from the reactions or transport have a minimal impact on flow during a numerical time step. Flow and transport equations should remain coupled, i.e., solved simultaneously, when solutes affect flow, as in the case of saltwater intrusion where concentration controls water density and viscosity and therefore flow (see Equation 3-2). Most of the processes considered here occur in dilute aqueous solutions, so decoupling is valid. Some remediation processes, such as in situ biotreatment, may be at least weakly coupled to flow since biomass can occlude pores and reduce permeability.

For nonreactive transport ($\Sigma R_k = 0$) and with constant and uniform velocity and homogeneous dispersivity, Equation 3-17 reduces to:

$$\frac{\partial C_i}{\partial t} = D_x \frac{\partial^2 C_i}{\partial x^2} - v_x \frac{\partial C_i}{\partial x} \qquad (3\text{-}18)$$

A number of analytical solutions have been developed for equations such as (3-18) for various types of boundary conditions. For example, Ogata (1970) developed a one-dimensional, analytical solution for a nonreactive solute transport from a step input function ($C(0,t) = C_0 \ t \geq 0$)] into a semi-infinite column ($C(\infty,t) = 0 \ t \geq 0$), initially devoid of solute ($C(x,0) = 0 \ x \geq 0$):

$$\frac{C}{C_0} = \frac{1}{2}\left[\mathrm{erfc}\left[\frac{x - vt}{2\sqrt{D_x t}}\right] + \exp\left[\frac{vx}{D_x}\right] \mathrm{erfc}\left[\frac{x + vt}{2\sqrt{D_x t}}\right] \right] \qquad (3\text{-}19)$$

where C_0 is the inflow concentration $(=C_W)$ and *erfc* is the complementary error function $\left(\mathrm{erfc}\,(x) \equiv \frac{2}{\sqrt{\pi}}\int_x^\infty e^{-u^2}\,du \right)$. Several compilations of analytical solutions are available for a wide range of simple transport problems (Wexler 1989, Javandel, Doughtry, and Tsang 1984, Yeh 1992, Beljin and van der Heijde 1993). Some of these analytical solutions to the ADT equation include solute retardation (see Chapter 5), first-order degradation, and other simple process or reaction terms, and therefore they may be useful in preliminary modeling of XAC transport.

Structured or heterogeneous porous media

Natural soils and sedimentary aquifer materials are intrinsically heterogeneous as described briefly in Chapter 2. Contaminant transport in heterogeneous or structured porous media is presently an active area of research. The unsatisfactory performance of remediation models based on traditional ADT concepts is forcing reevaluation and the development of more realistic (or less unrealistic) conceptual and mathematical models.

One of the more commonly applied conceptual models for structured media envisages a soil or sedimentary aquifer as a bicontinuum of high and low permeability zones. Advective transport dominates in the permeable mobile water zones, while diffusive transport dominates in the immobile water zone. The advection-dominated zones in soils are the macropores or inter-aggregate fractures, and the diffusive zones are the aggregate matrices. For sedimentary aquifers, the immobile zones could be lithic fragments in sand and gravels beds or fine-grained lenses within, or aquitards adjacent to, media of higher permeability. Variations of this two-region model concept have been applied at the scale of particle microfractures and soil aggregates up to the aquifer scale, at which the aquifer is conceptualized as an idealized heterogeneous or fractured porous media.

As long as flows are strongly contrasting between the two regions, this conceptualization of a bicontinuum of advective and diffusive zones appears to be reasonable. The difficulty in quantitating mobile and immobile region volumes or obtaining independent verification impedes general application of this conceptual model approach. There is no theoretical limit to the number of mobility regions that could be defined, representing a spectrum of permeabilities, but quantification and verification would remain difficult. Transport through moderately contrasting, heterogeneous media presents a greater

challenge in that both advective and diffusive mass transfer would occur between regions.

Molecular diffusion is a very slow process. Therefore, its significance in contaminant transport modeling appears to be dependent on the duration of the solute-media interaction and the scale of heterogeneities present. At the bench scale, small-scale heterogeneities (intraparticle, intra-aggregate) may be very significant. In groundwater contamination scenarios involving heterogeneous media, intraparticle diffusion may be virtually instantaneous relative to intra-strata diffusion. The contrast would increase at longer exposure times (more time to diffuse into low mobility zones). Since permeability heterogeneities exist at all scales, the most significant diffusion process (intraparticle, intra-aggregate, or intrastratum) can be expected to vary with the scale of investigation.

Mathematical formulations for two-region models are presented as part of the discussion of sorption processes (Chapter 5), since these models were developed primarily to describe the nonequilibrium transport of sorbing sol-utes. Models vary primarily in the form of the expression for the diffusive mass transfer between matrix and macropore. Early applications to soils borrowed conceptual models from the chemical engineering models for col-umn chromatography and packed bed reactors with porous catalysts.

Fractured porous media

Most consolidated porous media contain fractures, joints, or faults devel-oped sometime during their extended geologic history. Though fracture zones are typically perceived as conduits for flow, they may also act as barriers.

When conceptualizing flow through fractured media, one of four general approaches is usually adopted (van der Heijde, El-Kadi, and Williams 1988, Schmelling and Ross 1989):

a. Equivalent porous medium (EPM) or continuum concept.

b. Discrete fracture (DF) model.

c. Geometrically based (GB) model.

d. Stochastic fracture distribution models.

Few if any of the numerical models developed for transport in fractured media are field-validated for remediation applications and, therefore, should be con-sidered as research codes.

The EPM approach treats the fractured medium as if it were a porous medium, permitting application of traditional flow and transport equations. The EPM concept may be workable when fracture density is high relative to

spatial discritization in numerical modeling. High, fracture interconnectivity is also essential. This approach is more appropriate for water flux prediction (e.g., Pankow et al. 1986) than for solute transport simulation, since mass transfer between fracture and matrix is not considered. The multiple interacting continua (MINC) conceptualization of Pruess and Narasimhan (1985) extends the EPM approach to include mass transfer between well-connected high-permeability fractures and isolated matrix blocks of low permeability.

Discrete fracture (DF) models conceptualize flow and transport in the medium to be dominated by the fracture system. Flow is treated as flow between subparallel plates, the geometry of which may vary from parallel fractures to more complex, irregular, three-dimensional networks. Water and solute mass exchange with matrix is often neglected. If fracture density is relatively low and transport is dominated by fracture flow (low permeability matrix), then flow is treated as occurring in planar elements. The DF approach requires considerable field data since explicit delineation of fracture geometry and interconnectedness must be determined. The great difficulty in delineating the fractures in the field severely limits the utility of the DF approach.

In a GB conceptualization, the fractures and/or matrix blocks are conceptualized as having a regular geometry. This highly idealized conceptualization may be applicable for media in which regular subparallel fractures have been induced by relatively simple (i.e., few and uniform) regional stresses (e.g., tectonic, eustatic). van Genuchten and Dalton (1986) adopt a GB model to describe transport in aggregated soils; this topic will be reviewed with respect to physical nonequilibrium sorption processes (Chapter 5).

The stochastic approach predicts a fracture pattern by some random or semi-random means, perhaps conditioned on available field observations. Flow and transport could then be simulated with a discrete fracture approach.

3.4 Flow and Transport in Unsaturated Media

Unsaturated media include most soils and the vadose zone, defined as the region above the water table. Transport of explosives in unsaturated media is complicated, relative to saturated conditions, by additional potential processes:

   a. Saturation effects on flow and advection, e.g., the typically nonlinear and hysteretic saturation–permeability and saturation–pressure constitutive relations.

   b. Unique structural effects on advection, e.g., macropore flow.

   c. Saturation effects on dispersion (and other processes).

   d. Higher microbial biomass and activity.

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e. Dissolution/precipitation of constituents in response to
   wetting/desiccation cycles.

f. Relation to surface flow processes, e.g., precipitation, runoff,
   infiltration.

g. Volatilization and vapor transport; evapotranspiration.

The nonlinear and hysteretic nature of the unsaturated flow equations presents
the greatest challenge to both characterization and numerical modeling of the
systems.

Structured soils possess highly heterogeneous flow paths. Preferential flow
paths may be established along desiccation fractures, burrows, and root casts.
Relatively high microbial activity and high organic carbon and clay mineral
content of soils create an environment with potentially great impact on con-
taminants entering the subsurface directly from the soil horizon, as in the case
with many XAC-contaminated sites.

The amount of interstitial water in unsaturated media is described as the
proportion of either the total porosity (saturation, S_w) or the bulk volume of
the medium (water content, θ_w). Water saturation ranges from 0 to 1.0; mois-
ture content ranges between 0 and n (porosity). Preference for one or the
other terminology is largely discipline-dependent, but since soil scientists tend
to use θ_w, that convention is adopted here.

The conductivity (K) and intrinsic permeability (k) of the porous medium
are defined for saturated conditions ($\theta_w = n$). At lower saturations ($\theta_w < n$)
water flow becomes increasingly restricted, reducing the effective water con-
ductivity. The ratio of the saturation-dependent conductivity to the saturated
conductivity is the relative conductivity, K_{rw} ($= K(\theta_w)/K$). The typically
nonlinear relation between K_{rw} and θ_w arises from the fact that the larger,
well-connected pores (faster flow paths) drain relatively quickly as saturation
decreases. Drainage from progressively smaller pores is retarded by increas-
ingly retentive capillary pressure.

Common soil and aquifer materials are hydrophilic or water-wet, i.e.,
water tends to spread over the surfaces, displacing the nonwetting air phase.
Capillary pressure (P_c) is the pressure contrast between the nonwetting and
wetting phases across the meniscus at the vapor-liquid interface ($P_c =
P_{nw} - P_w$). The soil air phase pressure usually is assumed to be constant and
atmospheric ($P_{nw} = 0$; gage pressure), i.e., air flow and compressibility are
neglected. Therefore, under unsaturated conditions, capillary pressure is
negative. Capillary pressure may be described in terms of the surface tension
at the curved meniscus; as the water drains from ever smaller diameter pores,
the radius of curvature of the meniscus decreases and capillary pressure
increases, retarding the drainage.

The saturation-conductivity-pressure constitutive relations typically show hysteresis, e.g., conductivity is not a unique function of saturation but depends on the wetting-draining history of the medium. Hysteresis is neglected in most applications because: (1) practical process descriptors for this complex phenomenon are not readily available, and (2) the effects are commonly small relative to the impact of changes in the primary parameters in the constitutive relations. The best practice for now may be to characterize the constitutive relations separately for wetting and drying "limbs" of the curve; parameters generally will be different. Relative permeability is usually assumed to be isotropic, though this assumption is rarely substantiated experimentally.

Unsaturated flow

Unsaturated, vertical, seepage velocity may be described using a modified Darcy equation in which the unsaturated conductivity is a function of water content ($K = K(\theta)$) (de Marsily 1986):

$$q = -K(\theta)\,\frac{\partial h(\theta)}{\partial z}\tag{3-20}$$

Since water pressure (p) is negative for unsaturated conditions, the use of suction pressure, $\psi(\theta)$ ($= -p$), or matric potential head is more convenient. Expanding the definition of pressure head gradient in Equation 3-20, $\nabla h = \nabla(\psi(\theta) + z + p_{air}/\rho g)$, yields:

$$q = K(\theta\ or\ \psi)\left[\frac{\partial \psi}{\partial z} + 1\right]\tag{3-21}$$

When capillary pressure gradients are small relative to 1, $\partial \psi/\partial z$ is negligible and q approaches $K(\theta)$ (Charbeneau and Daniel 1992).

One-dimensional (vertical) flow in variably saturated porous media traditionally is described using the Richards equation (van Genuchten and Jury 1987, van Genuchten, Leij, and Yates 1991):

$$\frac{\partial \theta}{\partial t} = C(h)\,\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\left[\frac{\partial h}{\partial z} - 1\right]\right]\tag{3-22}$$

where $C(h)$ is soil water capacity [L^{-1}] defined by the slope of the water retention curve $\theta(h)$ or $d\theta/dh$, h is soil water pressure head [L], z is depth [L],

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$K(h)$ is the unsaturated hydraulic conductivity $[L \cdot T^{-1}]$ as a function of h, and t is time (T). Richards equation assumes that the vapor phase is passive.

Constitutive relations

The interdependence of water content (θ), capillary pressure or head (P_c, ψ), and conductivity ($K(\theta)$ or $K(\psi)$) constitutes the fundamental constitutive relations needed to describe unsaturated flow. These relations are fluid and medium dependent, and therefore should be determined experimentally. No reliable models have been developed to predict a priori these relations based on independent soil properties such as grain-size distribution. Several semi-empirical functions have been proposed to describe the ψ-θ, K-ψ, or K-θ relations (Hillel 1980):

$$
\begin{aligned}
K(\psi) &= a \,/\, \psi^{\,n} & (a) \\
K(\psi) &= a \,/\, (b + \psi^{\,n}) & (b) \\
K(\psi) &= K_s \,/\, [\, 1 + (\psi \,/ \psi_c)^{\,m} \,] & (c) \\
K(\theta) &= a\,\theta^{\,m} & (d) \\
K(\theta) &= K_s\, s^{\,m} = K_s\, (\theta \,/ f)^{\,m} & (e)
\end{aligned}
\qquad (3\text{-}23)
$$

where K_s is the saturated hydraulic conductivity, ψ_c is the matrix suction head at which $K = 0.5\, K_s$, f is porosity, s is saturation, and a, n, and m are fitted parameters, unique to each equation.

The more commonly used constitutive functions, at least in contaminant transport modeling, are the van Genuchten, Brooks-Corey, and the Campbell relations. Baek, Clesceri, and Clesceri (1989) also describe a sigmoidal function.

van Genuchten. The van Genuchten (1980) relation employs three fitting parameters (n, m, and α):

$$
\theta_e = \left[\frac{1}{1 + (\alpha h)^{\,n}} \right]^{m}
\qquad (3\text{-}24)
$$

where h is the pressure head, and θ_e is the effective water content defined as:

$$
\theta_e = \frac{\theta - \theta_r}{n - \theta_r}
\qquad (3\text{-}25)
$$

The effective water content is that saturation which is capable of flow, i.e., in excess of the immobile, residual saturation (field capacity, θ_r). Note that m = $(n-1)/n$ or = $(1 - 1/n)$. Relative conductivity is expressed as:

$$K(\theta)_r = \sqrt{\theta_e} \left[1 - \left[1 - \theta_e^{\frac{1}{m}} \right]^m \right]^2 \qquad (3\text{-}26)$$

Brooks-Corey. Brooks and Corey (1964) developed an expression for soil water saturation—capillary pressure which tries to capture the influence of the threshold entry pressure:

$$\theta_e = \left[\frac{h_b}{h} \right]^\lambda \qquad (3\text{-}27)$$

where h_b is the bubbling capillary pressure, i.e., the pressure required for the nonwetting phase (air) to displace water. The pore size distribution is represented by the λ parameter. Relative conductivity is described by:

$$K(\theta)_r = \theta_e^{\left(3+\frac{2}{\lambda}\right)} \qquad (3\text{-}28)$$

Campbell. Campbell (1974) developed a simple expression similar to the Brooks-Corey for θ-h :

$$\frac{\theta}{n} = \left[\frac{H_b}{h} \right]^{\frac{1}{b}} \qquad (3\text{-}29)$$

where H_b is a scaling parameter [L] analogous to h_b above, n is porosity, and b is a constant ($\approx 1/\lambda$). Relative conductivity is described by:

$$K(\theta)_r = \left[\frac{\theta}{n} \right]^{3 + 2b} \qquad (3\text{-}30)$$

Sigmoidal. Baek, Clesceri, and Clesceri (1989) utilize a sigmoidal expression for the constitutive relations "because of their adaptability to the full range of water content, particularly near the saturation point:"

$$\theta = \frac{a\ \theta_{max}}{a + (\epsilon - \psi)^b} \qquad (3\text{-}31)$$

and

$$K(\theta) = \frac{c\ K_{sat}}{c + (\epsilon - \psi)^d} \qquad (3\text{-}32)$$

where a, b, c, and d are fitted parameters, θ_{max} is the maximal water content (at saturation, i.e. porosity), K_{sat} is the saturated hydraulic conductivity, and ϵ is an "infinitesimal number."

Unsaturated transport

Transport processes in unsaturated media are essentially the same as in saturated transport. However, modifications in the process descriptors may be necessary to reflect: (1) the typically ready supply of oxygen, (2) macropore transport that can accelerate contaminant dispersal and bypass biogeochemically active soil zones, and (3) the medium that is susceptible to desiccation or freezing which could affect XAC transport.

Unsaturated transport is typically modeled with a Fickian-based advective-dispersive equation, just as with saturated transport, for example (van Genuchten and Jury 1987):

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z}\left[\theta D \frac{\partial C}{\partial z} - q C\right] \qquad (3\text{-}33)$$

For steady-state water content Equation 3-33 reduces to:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \qquad (3\text{-}34)$$

where terms are analogous to the saturated transport equation, except now $v = q/\theta$. Dispersion might be expected to be somewhat dependent on saturation, since at lower saturation flow paths could be more tortuous. Any such dependence is neglected typically since it would be difficult to quantitate and be site-specific.

The classical models for unsaturated flow and transport (Richards equation and Fickian ADT) are useful in predicting approximate behavior in soils. However, these formulations do not capture field scale influences of preferential flow through macropores or spatio-temporal variation of flow and process parameters (hysteresis; irreversible processes) (van Genuchten and Jury 1987).

3.5 Research Recommendations

Investigate XAC transport in unsaturated media. Most of the research involving explosives or XACs in porous media has been conducted in saturated porous media. Very little work has been conducted in unsaturated media. This fact is likely due to the experimental difficulties in controlling and monitoring unsaturated flow and transport. Yet, unsaturated media are obviously the most immediately impacted by XAC transport. Much more biogeochemical process research is needed to better understand XAC fate and transport. Some of that research should be conducted under unsaturated conditions which surely will exert some influence on types or rates of these biogeochemical processes.

Investigate the scale-dependence of dispersion in heterogeneous media. The use of a scale-independent, Fickian model for dispersion may be inappropriate in certain cases, such as in near-source regions or in heterogeneous media. Descriptors are needed to predict dispersion (and other transport processes) at all pertinent scales based on parameters derived from intrinsic media properties rather than those fitted to observations at various scales. The problem of scale-dependence is universal to all solutes and is not restricted to XACs.

4 Aqueous Solubility

The aqueous solubility of a compound is a fundamental property and a critical parameter in modeling its environmental fate and transport. Explosives associated compounds (XACs) are commonly present as crystalline solids mixed in soils and perhaps transported into the shallow subsurface. These low-solubility solids, if left in place, would dissolve slowly and leach into groundwaters. Many transformation processes affecting explosives are active primarily in the aqueous phase (e.g., biotransformation) and therefore may be limited by dissolution kinetics. A quantitative understanding of the multiple controls on solubility and dissolution/precipitation kinetics is necessary to predict loading rates (boundary conditions) to the subsurface from contaminated soils.

A brief review of thermodynamics and some fundamental principles involved in describing and/or estimating the solubility of solids follows in Section 4.1. Dissolution kinetics descriptors are presented in Section 4.2. The possible influence of non-XAC solutes or other groundwater constituents on the solubility and facilitated transport of contaminants is examined in Section 4.3. Finally (Section 4.4), the aqueous solubility of XACs is reviewed and recommendations for future research are presented.

4.1 Fundamental Principles

The solubility of a pure organic solid (compound 2) in water (compound 1) depends not only upon the interactions between the solute and solvent system, as reflected in the activity coefficient ($\gamma_{2(W)}$), but also on the standard state fugacity (f_2^o), defined as a reference for the activity coefficient, and the pure solid fugacity ($f_{2(S)}^o$). The fundamental condition for equilibrium in the partitioning of compound 2 (e.g., any XAC) between the crystalline and solute condition is the equality of solid (S) and aqueous phase (W) fugacities (f_2):

$$f_{2\,(S)} = f_{2\,(W)} \tag{4-1}$$

For a sparingly soluble (nonionic), organic solid in water, the fugacity of the pure solid ($f_{2(S)}$) is:

$$f_{2(S)} = \gamma_{2(W)} \, X_{2(W)} \, f_2^{\,o} \tag{4-2}$$

where $\gamma_{2(W)}$ is the aqueous activity coefficient, $X_{2(W)}$ is the mole fraction of 2 in the aqueous phase, and $f_2^{\,o}$ is an arbitrary, but precisely defined, standard state fugacity. A pure, supercooled liquid (SCL) form of component 2 at the temperature of interest is a convenient reference state $(f_{2(SCL)}^{\,o})$:

$$f_2^{\,o} = f_{2\,(SCL)}^{\,o} \tag{4-3}$$

The SCL condition is a hypothetical state in which the dissolving compound is a liquid. This conceptualization permits resolution between the process of mass transfer into the solvent and the dissociation from the crystalline structure.

Substituting Equation 4-3 into Equation 4-2 and rearranging, it is evident that the aqueous mole fraction $X_{2(W)}$, a parameter to be predicted, varies inversely with the activity coefficient, and directly with the fugacity ratio (Prausnitz, Lichtenthaler, and de Azevedo 1986, Prausnitz et al. 1980):

$$X_{2(W)} = \left[\frac{1}{\gamma_{2\,(W)}} \right] \left[\frac{f_{2(S)}^{\,o}}{f_{2(SCL)}^{\,o}} \right] \tag{4-4}$$

Yalkowsky and Banerjee (1992) express Equation 4-4 in terms of the solubility ratio of the crystalline solid (X_C) to the supercooled liquid (X_{SCL}):

$$\log X_{2(W)} = \log \left[\frac{X_C}{X_{SCL}} \right] - \log \gamma_{2(W)}^{\infty} \tag{4-5}$$

where X_C is the aqueous solubility (mole fraction) of the crystalline solid, X_{SCL} is the solubility of the SCL, and $\gamma_{2(W)}^{\infty}$ is the activity coefficient at infinite dilution.

Crystallinity effects on solubility may be described by the van't Hoff equation:

$$\log \left[\frac{X_C}{X_{SCL}} \right] = -\frac{\Delta S_f (T_m - T)}{2.303 \; R \; T} + \frac{\Delta C_p (T_m - T)}{2.303 \; R \; T} - \frac{\Delta C_p \log \left[\dfrac{T_m}{T} \right]}{R} \tag{4-6}$$

where ΔS_f and ΔC_p are, respectively, the changes in entropy and heat capacity between the crystalline and liquid (SCL) forms (Yalkowsky and Banerjee

1992). The T_m and T are the melting point and system temperatures [°K], respectively.

For "large" molecules with many bonds to attenuate energy of temperature changes, ΔC_p is approximately 0, and the solubility ratio (X_2^C/X_2^{SCL}) may be approximated with:

$$\log \left[\frac{X_C}{X_{SCL}} \right] = - \left[\frac{\Delta S_f (T_M - T)}{2.303 \; R \; T} \right] \qquad (4\text{-}7)$$

For "small" molecules with relatively few bonds, increase in bond vibration with temperature has minimal effect on ΔC_p, and the ΔC_p upon melting is similar to an entropy change, approximated by ΔS_f (Hildebrand, Prausnitz, and Scott 1970, Yalkowsky and Banerjee 1992). If $\Delta C_p \approx \Delta S_f$, Equation 4-6 reduces to:

$$\log \left[\frac{X_C}{X_{SCL}} \right] = - \frac{\Delta S_f}{R} \log \left[\frac{T_m}{T} \right] \qquad (4\text{-}8)$$

Equations 4-7 and 4-8 give similar estimates at environmental temperatures for low melting point solids (explosives have low to moderate melting points, most less than 205 °C). Yalkowsky and Banerjee (1992) report a typical value for ΔS_f of 13.5 e.u. for large, rigid molecules. Thus for large, rigid molecules at 25 °C, Equation 4-5 becomes:

$$\log X_{2(W)} \approx 0.25 - 0.01(MP) - \log \gamma_{2(W)}^{\infty} \qquad (4\text{-}9)$$

where MP is the melting point in °C (versus M_T in °K). Modification of Equation 4-9 to conform to empirical relations between aqueous solubility and the octanol/water partitioning coefficient (K_{ow}), as derived from the Hansch group contribution method, yields (Yalkowsky and Banerjee 1992, p 53):

$$\log S_W = - 0.01 (MP - 25) - \log K_{ow} + 0.8 \qquad (4\text{-}10)$$

where S_W is the molar aqueous solubility of the solid. Note that solubility tends to decrease as melting point increases.

Temperature effects. The solubility of solids tends to increase with temperature as suggested by Equations 4-7 and 4-8. However, increasing temperature may also increase the activity coefficient of the solute (Walas 1985), which will have the effect of decreasing the solubility, as indicated by Equation 4-5. The solubility of solids tends to be much more sensitive than organic liquids to temperature (Yalkowsky and Banerjee 1992).

Mixed solvents. The aqueous solubility of hydrophobic, organic solids tends to increase in the presence of other dissolved organic solvents (cosolvents) in the aqueous phase. Cosolvency phenomena are discussed in Section 4.3.

Mixtures of solids. The solubility of components in solid mixtures is poorly understood, but Banerjee (1984) suggests that as long as the components behave ideally (e.g., not a solid solution), the solubility behaviors are independent. Military explosives are commonly physical mixtures, not solid solutions.

Free energy and solubility. Dissolution is essentially a mixing process that must be accompanied by a decrease in the Gibbs energy, ΔG^o_{soln}, which is governed by changes in enthalpy (ΔH^o_{soln}) and entropy (ΔS^o_{soln}):

$$\Delta G^o_{soln} = \Delta H^o_{soln} - T \Delta S^o_{soln} \tag{4-11}$$

at constant pressure and temperature (Yalkowsky and Banerjee 1992, Prausnitz et al. 1986). A decrease in Gibbs energy ($\Delta G_{soln} < 0$) and solubility tends to be enhanced by lower enthalpy (more exothermic), an increase in entropy, and/or an increase in temperature.

4.2 Dissolution/Precipitation Kinetics

Dissolution of molecular crystals (e.g., most explosives solids) involves breakage of relatively weak van der Waals bonds (Adamson 1982). Molecular crystals are those comprised of an ordered arrangement of nonionic molecules. A simple dissolution "reaction" may be described as:

$$TNT_{xal} + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} TNT^o + H_2O \tag{4-12}$$
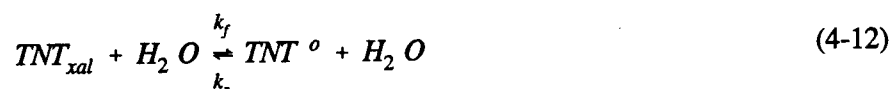
where the subscript "*xal*" indicates a crystalline reactant, the superscript "*o*" indicates an uncharged solute, and the k_f and k_r are forward and reverse reaction rate constants. Solubility describes the maximum aqueous concentration in equilibrium with the solid ($k_f = k_r$). Dissolution into an aqueous phase, unsaturated with respect to the crystalline material (i.e., $C_{bulk} < C_{sat}$ and $k_f > k_r$), necessarily involves diffusive transport, and usually advective transport, to move newly dissolved molecules from the solid-water interface into the bulk solution.

Mathematical descriptors for the dissolution kinetics of crystalline solids commonly conceptualize a system in which the aqueous phase at the solid-water interface is saturated with respect to the solute. A Fickian diffusion model is commonly evoked to describe the mass transfer across a boundary

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layer into the bulk aqueous phase. This model requires a mass transfer coefficient and some estimate of the film thickness. Intuitively, the film thickness varies inversely with the flow velocity in the pore but is not easily measured. Thus, most dissolution kinetics models are largely empirical. For example, Yalkowsky and Banerjee (1992) present the general expression of Noyes and Whitney (1897) for the dissolution rate, Dr [$M \cdot L^{-2} \cdot T^{-1}$]:

$$Dr = \frac{D A_s (C_o - C)}{h V} \tag{4-13}$$

where D is the diffusion coefficient [$L^2 \cdot T^{-1}$], C is the bulk aqueous concentration [$M \cdot L^{-3}$], and C_o is the aqueous concentration at the solid surface [$M \cdot L^{-3}$] in chemical equilibrium with the solid of surface area A_s [L^2] and total volume V [L^3]. Mass transfer occurs over the surface area A_s into the boundary layer. The constant h [–] is dependent upon the aqueous solution viscosity and mixing conditions, i.e., the empirical parameter taking into account the influence of flow velocity on film thickness. For a well-mixed reactor or well-flushed porous medium (i.e., high advection and sweep efficiency), in which the interface concentration is saturated with respect to the compound ($C_o = C_{sat}$), and the bulk concentration taken to be zero or negligible, Equation 4-13 reduces to:

$$Dr = \frac{D A_s C_{Sat}}{h V} \tag{4-14}$$

Stumm and Morgan (1981, p 315) describe dissolution (precipitation) kinetics in terms of aqueous concentration:

$$\frac{dC}{dt} \approx k A_s (C_o - C) \tag{4-15}$$

where k [$L^{-2} \cdot T^{-1}$] is a rate coefficient. They suggest that Equation 4-15 describes the limit for diffusion-limited dissolution (or growth). Dissolution may also be limited by surface kinetic processes, for which Stumm and Morgan (1981) present the expression:

$$\frac{dC}{dt} = k' A_s (C_o - C)^n \tag{4-16}$$

where k' (versus k in Equation 4-15) is a rate coefficient and n (–) is the order of the reaction (e.g., $n = 2$ for $CaCO_3$, = 1 for KCl).

Equations 4-13 to 4-16 indicate that the rate of dissolution is directly proportional to the available particle surface area. Thus, dissolution rates are

expected to be greatest for smaller particles in contact with pristine ground-waters flowing at high velocity.

Solubility is governed by differences in free energy between solid and dissolved conditions (ΔG), whereas dissolution kinetics is regulated by the free energy contrast between the solid and the transition state, ΔG_A (Yalkowsky and Banerjee 1992). Even dissolution that is thermodynamically favored ($\Delta G < 0$) may be impeded by the high activation energy required. This kinetic barrier in the dissolution of solids arises from the energy needed to break bonds, however weak, in the crystalline structure.

Free energy in the solid phase is related inversely to the degree of order or crystallinity in the solid. Even if two solutes have similar energies in solution and similar activation energies, the free energy in the solid phase may be different. Consider the three-ring polynuclear aromatic solids anthracene and phenanthrene; anthracene is linear and symmetric whereas phenanthrene has a nonlinear structure. Phenanthrene with the higher energy in the solid phase (more disordered crystal structure; lower density) will dissolve faster, other factors being equal (Yalkowsky and Banerjee 1992).

Dissolution of mixtures of solids may become increasingly incongruent if constituents have strongly contrasting solubilities, developing a physical (diffusive) barrier to the more soluble components. Imagine a homogeneous, spherical aggregate of two solids: component A is slightly soluble, and component B is negligibly soluble. The aggregate is bathed in solvent at the outer surface. Dissolution of the more soluble A will progress inward from the outermost regions. Dissolution of the much less soluble B will precede likewise, but as a slower rate. As dissolution progresses, the distance increases between the water—A interface to the aggregate's margin, imposing an increasingly severe diffusion barrier. Conversely, the surface area of B increases as A is dissolved.

4.3 Facilitated Transport

Facilitated transport (FT) and chemically enhanced solubilization (CES) are general terms for a group of mechanisms by which the mobility of contaminants is increased. It is not uncommon for reported aqueous concentrations of highly hydrophobic organic contaminants (HOCs) to exceed their solubility limit or the level expected after equilibrium sorption partitioning onto soil solids (see Chapter 5). The apparently anomalous concentrations usually are due to field deviations from the conditions under which the aqueous solubility was determined (i.e., single solute in pure water). The elevated concentrations may be real, i.e., enhanced partitioning into the aqueous phase due to the influence of dissolved cosolvents or macromolecules. Alternatively, the anomalous concentrations may be an artifact of improper sample collection and/or analysis, e.g., the HOC may have been sorbed to mobile colloidal particulates which were not filtered out prior to chemical analysis. Either

mechanism can facilitate transport naturally or may be engineered to accelerate remediation technologies that rely on advective transport to remove sorbing solutes, e.g., pump-and-treat.

Cosolvency

The solubility of organic contaminants tends to increase with dissolved organic carbon (DOC) concentration (Huling 1989, Suffet and MacCarthy 1989, Pinal et al. 1990, Yalkowsky and Banerjee 1992). The DOC compounds are acting as cosolvents or complexing macromolecules to enhance the hydrophobic contaminant's partitioning into the aqueous phase. Many cosolvents occur naturally such as humic and fulvic acids. Certain compounds in multicomponent contaminants may act as cosolvents (e.g., ethanol in gasoline). Likewise, the action of cosolvents can be utilized in subsurface remediation.

Predicting cosolvency effects on XACs requires the modeling of multicomponent solid-liquid equilibria for the explosive(s)-cosolvent(s)-water system. Unfortunately, the database for XAC interactions is much less developed than for more common organic or inorganic solutes. The two general modeling approaches are: (1) empirical or statistical QSPRs such as the log-linear model, or (2) estimating activity coefficients for these commonly nonideal systems (UNIFAC).

Pinal et al. (1990) evaluated the effects of completely miscible organic solvents (CMOS; e.g., methanol, acetone) and partially miscible organic solvents (PMOS; e.g., nitrobenzene, toluene, TCE) on the aqueous solubility of hydrophobic organic compounds (HOC; e.g., naphthalene). Nonpolar PMOSs did not appreciably increase HOC solubility, but polar PMOSs such as nitrobenzene did increase solubility. Pinal et al. contended that the effect of polar PMOSs is due to their greater solubility (and molar volume). Cosolvency effects of the CMOSs increased with decreasing polarity (opposite for PMOSs). Two popular, organic equilibrium models—the log-linear model and the UNIFAC model—were applied to the ternary systems investigated and compared to observations of cosolvency.

Log-linear model

The log-linear model of Yalkowsky and Roseman (1981) relates the solubility of HOCs (subscripted h) in a mixture ($S_{h/mix}$) of N cosolvents to a weighted average of the logarithms of the HOC's solubilities in the pure solvents ($S_{h/n}$):

$$\log \frac{S_{h/mix}}{S_{h/w}} = \sum_{n=1}^{N} \sigma_{s/n} \, f_n \qquad \text{(4-17)}$$

where $S_{h/w}$ [M·L⁻³] is the aqueous solubility. The cosolvency power, $\sigma_{s/n}$, is the log of the ratio of pure solvent solubility to water solubility: $\log (S_{h/n}/S_{h/w})$. The volume fraction of cosolvent n in the mixture (f_n) is the weighting factor. Several assumptions are made in the development of the log-linear model:

a. Volume fractions are adequate weighting factors, which implies that CMOS-water and PMOS-water interactions are similar.

b. CMOS-PMOS interactions are negligible.

c. Volume fractions are additive (ideal mixing).

d. In biphasic systems (two liquid phases), no water or CMOS partitions into the PMOS-rich phase.

In a water-CMOS-PMOS mixture, the HOC solubility $(S_{h/mix})$ would be:

$$\log \frac{S_{h/mix}}{S_{h/w}} = \sigma_{h/c} \, f_c + \sigma_{h/p} \, f_p \qquad (4\text{-}18)$$

where the subscripts c and p refer to the CMOS and PMOS, respectively. Since by definition the PMOS has a solubility limit, there is a maximum volume fraction value for f_p in a given CMOS-water mixture:

$$f_{p,\,max} \approx \left[\frac{S_{p/w}}{\rho_p} \right] 10^{(\sigma_{p/c} \, f_c)} \qquad (4\text{-}19)$$

where ρ_p is the PMOS density [M·L⁻³].

Applying the log-linear model to explosives is fairly straightforward. Explosives contaminants would be designated as HOCs. CMOSs could include natural, dissolved organic carbon (DOC) materials (e.g., acetic or humic acids) or cosolvents to enhance pump-and-treat operations (e.g., ethanol). The polar PMOS contaminants acting as weak cosolvents could be some XAC co-contaminants (e.g., nitrobenzene). Data on DOC solubilities would be required on a site-specific basis as this class of organic compound includes a variety of compounds.

UNIFAC model

The UNIFAC (UNIQUAC (functional-group activity coefficient)) model is a group-contribution model for the estimation of activity coefficients in multi-component mixtures of nonionic, organic chemicals. It is based on the universal quasi-chemical (UNIQUAC) equations and the solution-of-groups concept (Prausnitz et al. 1980). Group contribution models treat

multicomponent mixtures as solutions of a finite number of functional groups rather than mixtures of individual compounds (for which there are an infinite number of combinations).

The activity coefficient (γ_i) of component i in a mixture is comprised of a combinatorial part (γ^c) and residual part (γ^r):

$$\ln \gamma = \ln \gamma^c + \ln \gamma^r \tag{4-20}$$

The combinatorial part accounts for nonidealities introduced by geometrical effects (molecule size and shape). The residual part accounts for non-idealities due to interaction of functional groups. Advantages of the UNIFAC approach include:

  a. Versatility; parameters are available for most functional groups of interest.

  b. Multicomponent mixtures (including water and polar organic) are accommodated.

  c. Applicable to liquid-liquid (LLE), vapor-liquid (VLE), and liquid-solid (LSE) equilibrium calculations.

  d. Assumptions of the log-linear model (a-d) are relaxed.

The disadvantages of UNIFAC applied to environmental problems include:
(a) the inability to distinguish isomers (e.g., 2,4-dinitrotoluene and 2,6-dinitrotoluene), a limitation for all group-contribution models; and
(b) tendency to underestimate aqueous solubility for highly hydrophobic organics ($S_{h/w} < 0.01$ mg L^{-1}, as for many pesticides but not explosives compounds). A detailed discussion of the UNIFAC/UNIQUAC equations is beyond the scope of this review. For details concerning the derivation of these models, see Fredenslund, Jones, and Prausnitz (1975), Fredenslund, Gmehling, and Rasmussen (1977), and Prausnitz et al. (1980). For discussions or applications of UNIFAC in the prediction of cosolvency effects, see Pinal et al. (1990) and Yalkowsky and Banerjee (1992).

Several other group-contribution models have been developed to estimate activity coefficients, phase behavior, and equilibrium partitioning in mixtures of nonionic organics. In addition to UNIFAC/UNIQUAC there are:
(a) NRTL: Non-Random Two-Liquid model (Renon et al. 1971, Renon and Prausnitz 1969), and (b) ASOG: Analytical Solution of Groups (Tochigi, Hiraga, and Kojima 1980). All of these models were developed in the chemical engineering field for process design. Of the three, UNIFAC has been applied much more frequently to estimate environmental behavior of complex mixtures of organics.

Macromolecules, colloids, and micelles

Natural waters may contain a wide variety of organic constituents reflecting local biogeochemical processes. A broad spectrum of solubilities, molecular sizes, and constituent functional groups is typically represented in these complex mixtures. The distinction between a "true" solute molecule and a suspended, organic particulate is actually gradational and any classification based on size is arbitrary. Yet some classification scheme is necessary for the purposes of description and numerical simulation. Molecule sizes are typically on the order of 10^{-10} to 10^{-9} m (1-10Å), but macromolecules can range to above 10^{-8}m (100Å). Colloids are typically considered to be particulates less than 10 μm (10^{-5} m) in diameter, approximately corresponding to an aqueous settling velocity less than 0.01 cm·s^{-1}. The low end of the colloid size range is less well defined, but extends to around 5 x 10^{-9} m (Stumm and Morgan 1981, p 647). Micelles and microdispersed oil droplets also can be classified as colloids.

Macromolecules. Soluble macromolecules (e.g., humic and fulvic acids) can enhance the apparent aqueous solubility and subsequent transport of both organic and inorganic contaminants (Suffet and MacCarthy 1989, Chiou et al. 1986). Enfield and Bengtsson (1988) and Enfield, Bengtsson, and Lindqvist (1989) observe that macromolecules may travel through porous media faster than some conservative (and smaller) solutes such as tritiated water. Macromolecules appear to move preferentially along the more open (and high velocity) pore spaces because steric hindrances preclude the macromolecule from penetrating more restrictive pores where flow is slow. Reducing the porosity by increasing the clay content impedes the macromolecule relative to the conservative tracer.

Colloids. Organic and inorganic colloids are reported to enhance the subsurface transport of radionuclides, metals, and organic solutes (McCarthy 1990, McCarthy and Wobber 1993). Inorganic colloids include silica and a variety of oxyhydroxides of common metals (e.g., iron, magnesium, aluminum, manganese). Organic colloids include: (a) macromolecules such as humic substances and proteins; (b) biocolloids such as bacteria, viruses, and spores; and (c) nonaqueous phase liquids such as micelles.

Micelles and emulsions. Micelles or microemulsions are microscopic assemblages of amphipathic molecules which, when present above a critical concentration, can form dynamic aggregates or micellar colloids. The polar ends of the molecules orient to contact the enveloping water; the nonpolar ends orient toward the interior of the micelle. Hydrophobic contaminants can partition preferentially into micelles, associating with the nonpolar (interior) portions of the molecules. Microemulsions are distinct from emulsions (or macroemulsions) in that microemulsions are thermodynamically stable and reproducible. Emulsions are systems of two liquid phases separated by an interface at which amphipathic molecules are usually present. The amphipathic surface active agents (surfactants) tend to stabilize the emulsion.

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Descriptors for physicochemical facilitated transport

Descriptors for mechanically enhanced solubility (versus solute enhanced with cosolvents) due to the influence of either macromolecules, colloids, or micelles are all based on partitioning. Beyond this common basis, each mode is subject to unique processes controlling its environmental fate. Transport equations for colloids or macromolecules would be required. As indicated by the observations of Enfield, Bengtsson, and Lindqvist (1989), unusual transport phenomena may be active. Some suspended substrates may move faster than expected, others may be filtered out or adsorbed.

Sorption processes are involved in contaminant partitioning to the colloids or macromolecules, as well as to these substrates sorbing to the soil medium. Sorption descriptors are presented in Chapter 5. Micellar partitioning may be treated as a liquid—liquid partitioning process for which one of the solubility models introduced above might be appropriate. Contaminant transport in micelles or emulsions through porous media is not well understood.

4.4 Aqueous Solubility of Explosives

Aqueous solubilities for the common explosives range between 5 and 400 mg·L^{-1}, or, in molarity terms, between 0.016 and 3.170 mmol·L^{-1} (see Table 4.1). Aqueous solubility data are available for the more common, pure components, in pure water, at environmental (15-30 °C) or higher temperatures. Very limited data are available for the following:

a. Solubilities of non-munition XACs (e.g., production wastes, transformation products).

b. Dissolution kinetics for pure or mixed systems.

c. Precipitation kinetics in pure or mixed systems.

d. Cosolvency phenomena in natural or engineered, complex mixtures.

e. Solubility at reduced temperatures ($\leq$ 15 °C), common in the subsurface and cold regions soils.

Available information for several of these knowledge gaps is addressed below. Interrelations between dissolution and processes to which it may be coupled, such as sorption, evapotranspiration, or biotransformation, are largely unexplored.

Dissolution of explosives

Little data are available on the environmental dissolution kinetics of explosives or XACs. Soils and the vadose zone are wet cyclically during

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Table 4.1
Aqueous Solubility of Representative, Common Explosives, Associated Compounds, and Others (for comparison)

Compound[1]	Aqueous Solubility[2] S_w (mg·L⁻¹)	Molecular Weight MW (g·mol⁻¹)	Saturated Molarity (mmol·L⁻¹)	Melting Point MP (°C)	Dipole Moment[D] μ_{dm} (D)
2,4,6-TNT[R]	150.	227.13	0.660	80.75	1.37
2,4-DNT[R]	280.	182.14	1.540	72.	–
2,6-DNT[R]	208.	182.14	1.142	66.	–
1,3,5-TNB[R]	385.	213.11	1.807	122.	≈ 0.0 (sym)
1,3-DNB[R]	533.	168.11	3.170	90.	–
Nitrobenzene[R]	1900. (20 °C)	123.1	15.43	5.8	4.22 ±0.84
RDX[R]	45.	222.6	0.202	205.	≈ 0.0 (sym)
HMX[R]	5.	296.2	0.016 9	286.	≈ 0.0 (sym)
Tetryl[R]	80.	287.17	0.279	129.5	–
Picric Acid[R]	≈ 12,400.	229.12	54.120	123.	–
Water[D]	10.⁶	18.01	55.5 (mol./L)	0.0	1.85 ±0.1
Benzene[D]	1,780. (20 °C)	78.11	22.790	5.5	0.0 (sym)
Toluene[D]	~ 571	92.1	6.200	- 95.1	0.36 ±0.01
TCE[D]	1,100	131.5	8.365	- 87	–

[1] Superscript letters indicate references: D = Dean (1985), R = Rosenblatt et al. (1989).
[2] Aqueous solubilities at 25 °C unless otherwise stated.

infiltration events. Water in contact with soil XACs between recharge events would be more likely to approach saturation with respect to the XACs because of the longer contact times. Subsurface infiltration events would flush these solutes; continued inflow would have too little contact with explosive solids to approach equilibrium. Therefore, XAC loading to the subsurface from soils contaminated with crystalline XACs is expected to be episodic, but may be approximated as a steady flux if rainfall distribution (temporally and spatially) is fairly uniform.

Soils contaminated with chunks of mixed explosives or explosives within soil aggregates may require descriptors for incongruent dissolution (Section 4.2), which would entail a diffusion-limited mass transfer model similar

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to those discussed in Chapter 5. The munition Composition-B is a 60:40 physical mixture of RDX and TNT; TNT solubility is greater than RDX (150 mg L^{-1} versus 60 mg L^{-1}, respectively).

The XAC solutes in unsaturated soils or the vadose zone could conceivably precipitate or "salt out" if sufficient water is removed by evapotranspiration or soil water freezing. However, in a typical complex soil system containing a nonuniform distribution of contaminants, a variety of sorptive substrates, and relatively high microbial activity, the likelihood that soil waters will approach the solubility limit is remote.

Facilitated transport of XAC's

Any of these facilitated transport mechanisms discussed in Section 4.3 could affect explosives transport, although few have been documented as yet for XACs. It is quite likely that these processes have been overlooked, misinterpreted, or assumed to be of negligible influence.

Facilitated transport may be important for both the natural transport of XACs and for in situ remediation technologies. For example, enhanced biotreatment involves injection of organic solutes (e.g., acetate, biodegradable surfactants) which may, perhaps by design, facilitate solubilization and transport. Kaplan and Kaplan (1982) reported aqueous complexation of TNT with amino surfactants at alkaline pH's to form less soluble precipitates. However, other surfactants may prove to be a means by which to enhance solubility and bioavailability (Chapter 7).

Solubility of adsorbents or catalysts

Sorption (Chapter 5) and abiotic reactions (Chapter 8) are two important influences on the subsurface transport of XACs. The solubilities of several natural sorbents and possible catalysts are sensitive to variation in geochemical conditions, particularly with respect to pH, redox potential, and DOC compounds.

Extractable iron is a soil constituent that has been correlated with sorption of TNT and RDX (Pennington 1988, Ainsworth et al. 1993). Metal oxyhydroxides (e.g., $FeO(OH)$) as well as organic polymers (e.g., soil humics) may occur in subsurface media as both immobile grain coatings and mobile colloids. These materials tend to have large surface area to volume ratios and thus may influence the transport of sorptive contaminants to an extent disproportionately greater than their relative mass. As immobile precipitates, these materials can act to retard contaminant transport. As mobile colloids or microparticulates, the net effect can be to increase apparent solubility and enhance contaminant mobility.

The thermodynamic controls on the solubility of common oxyhydroxides of redox-sensitive metals (e.g., Fe, Mn) are fairly well understood—solubility increasing for the reduced species at low Eh and pH. If redox conditions were to be decreased sufficiently to dissolve the hydroxide substrates, any sorbed XACs or metals would be remobilized. Consideration of geochemical controls on oxyhydroxide behavior also may be required in order to avoid undesirable effects such as pore clogging by precipitating hydroxides or mobilized colloids. The reduced permeability effect could be misinterpreted as biofouling in the case of subsurface injection of electon acceptors (oxygen or peroxide).

Several thermodynamic (equilibrium), geochemical models are available to calculate inorganic (and some organic) solubility, speciation, and sorption as a function of Eh, pH, ion activity, and temperature (e.g., WATEQ4F, MINTEQA2, EQ3/6, PHREEQC, HYDROGEOCHEM, SOLMNEQ.88). Bassett and Melchior (1990) provided an overview and discussion of recent advances in geochemical modeling.

4.5 Research Recommendations

Additional research effort is needed into the following aspects of XAC solubility:

Determine aqueous solubility of key XAC's. Solubility data for numerous transformation product XAC's are not available. Before transport of these components can be simulated, physical properties must be measured or estimated. Explore group contribution type models or other approaches for estimating aqueous solubility of poorly characterized XACs (amino, azo, and azoxy compounds).

Investigate dissolution kinetics of pure and mixed explosives. There are very little data on this topic. Realistic, environmental, dissolution kinetics data are needed to evaluate solute source terms (boundary conditions) for groundwater models.

Evaluate the influence of cosolvents on XAC dissolution and facilitated transport. This research could be valuable in assessing both natural and remediation-based facilitated transport.

Evaluate the influence of colloidal and macromolecules in facilitated transport of XAC's.

Investigate the utility of geochemical models to evaluate the controls on the solubility of inorganic soil components that may affect XAC fate and transport. This tool will become invaluable once the soil component(s) responsible for XAC abiotic reductions, polymerization, and/or covalent binding are identified.

5 Sorption

The interactions between explosives associated contaminants (XACs) and porous media solids include both physical and chemical processes that significantly affect XAC fate and transport in the subsurface. Process descriptors are reviewed below for equilibrium and nonequilibrium, reversible and irreversible, sorption phenomena. A very broad definition of sorption is adopted here, referring to all XAC-solid interactions exclusive of dissolution/precipitation (Chapter 4) and surface catalyzed, irreversible reactions (Chapter 8).

5.1 Sorption Concepts

Adsorption and desorption

Adsorption is the dynamic process by which dissolved, chemical species (solutes) accumulate at an interface. Interfaces of potential interest in groundwater contaminant transport exist between water and (a) immobile solid particles (e.g., soil grains) other than XAC solids, (b) mobile solid particles (e.g., non-XAC colloids), (c) the air or vapor phase in unsaturated media, or (d) discrete accumulations of contaminant (e.g., crystalline XACs or nonaqueous phase liquids, NAPLs). The emphasis here will be on solute-solid interactions (immobile and mobile solid particles). The air-water interface is discussed in reference to volatilization processes (Chapter 6). Solvent-crystalline XAC interactions are reviewed in the discussion of solubility (Chapter 4); the solute-NAPL interface is not particularly pertinent to explosives transport and is not reviewed. Adsorption to solids may occur from any fluid phases present in the porous medium—aqueous, vapor, or NAPL. Only sorption from the aqueous phase is considered here, since vapor transport of most XACs appears to be minimal, and association with a NAPL is not common.

The adsorption process is generally reversible, and the reverse process is desorption. At equilibrium the local rates of adsorption and desorption are balanced. Irreversible "sorption" implies the formation of stable, covalent bonds between solute and solid. Irreversible sorption is discussed below as a

complication in the modeling of the sorption process, but is reviewed specifically as an abiotic reaction in Chapter 8.

Adsorption of a solute molecule from aqueous solution conceptually may involve several steps: (a) removing the solute from solution, including removal of any hydration waters; (b) removing sorbed water or other sorbates from the surface to which solute will adsorb; (c) transport of the molecule to a sorbent site or surface, which will be impeded by diffusion through pore waters and/or surface coatings; and (d) adsorption reaction or bond formation (Stumm and Morgan 1981). Rigorous modeling of the process would require consideration of each step of the process to determine which is rate limiting.

Soil and aquifer solids may possess microfractures or dissolution pits; other solids are naturally microporous materials (e.g., plant matter, zeolite minerals). Entry of solute into these micropores regardless of any specific interaction with the internal surface is the physical process of absorption. Waters within micropores are essentially immobile, constrained by high tortuosity and surface drag or the dead-end nature of the micropore. Thus, any mass exchange with external waters (mobile) or mass transport within the microporous material is by molecular diffusion.

Subsequent use of the term sorption refers to the combined effects of absorption and adsorption/desorption processes. Adsorption and absorption processes are difficult to resolve without carefully designed experiments at the bench scale. Field-scale experiments and modeling rarely resolve these processes.

Sorption can exert a pronounced effect on other transport processes affecting XACs. Diffusive transport into low permeability zones clearly will retard advective transport. Contaminants sorbed strongly or sorbed within microporous material may be chemically and/or physically unavailable for microbial transformation. The partitioning affects other medium-dependent, abiotic processes such as hydrolysis. Advection, dispersion, diffusion, sorption, biotransformation, etc., are actually coupled processes in that each may affect the rate of the others. The coupled nature of these processes has only recently begun to be appreciated.

The sorbent (substrate) material may be framework or cementing minerals, amorphous grain coatings of metal-oxyhydroxide or humic material, mobile colloids (organic or inorganic), or microbes. The diversity of available substrates and their structures in natural soils suggests that multiple sorption mechanisms may require consideration in the development of sorption descriptors. The nature of these associations and magnitude of partitioning between solution and substrate ultimately depend on the physicochemical properties of both the solute and the substrate and their response to complex and variable environmental conditions.

Local equilibrium assumption

Sorption process descriptors for contaminant transport and remediation modeling ultimately must be incorporated into the advection-dispersion expressions. One-dimensional, advective-dispersive transport with sorption in a saturated, homogeneous, incompressible, porous medium may be described by:

$$\frac{\partial C_i}{\partial t} = D_x \frac{\partial^2 C_i}{\partial x^2} - v \frac{\partial C_i}{\partial x} - \frac{\rho_b}{n_T} \frac{\partial S_i}{\partial t} \qquad (5\text{-}1)$$

where C_i is the aqueous concentration of solute i [$M_i \cdot L^{-3}$], t is time [T], v is seepage velocity [$L \cdot T^{-1}$], ρ_b is the bulk density of the solid medium [$M_s \cdot L^{-3}$], n_T is total porosity (assume $n_T = n_e$), and S_i is the mass of i per mass of dry solids [M_i/M_s]. Equation 5-1 has two unknowns, C_i and S_i, so another equation involving one or both variables is necessary to develop a solution. In most cases of interest the second equation is a relationship called a sorption isotherm relating S_i and C_i. The $\partial S_i/\partial t$ term in Equation 5-1 is the focus of sorption process descriptors. The multitude of available sorption models, much too numerous to review completely here, have been developed to describe various aspects of how solute partitioning varies with time, solute and sorbent concentration, the physical and chemical nature of the sorbate-sorbent system, and advective-diffusive processes. Several modeling approaches deemed applicable to explosives cleanup are reviewed here.

The local equilibrium assumption (LEA) is the cornerstone of traditional, groundwater transport and geochemical models currently available. The LEA is based on the assumption that groundwater flow is sufficiently slow relative to any reaction kinetics (e.g., solute complexation or speciation, adsorption, dissolution/precipitation), that local process equilibrium can be considered instantaneous. Sorption isotherms assume equilibrium conditions. The LEA is justified in many cases, such as the advective transport of weakly sorbing solutes under low, natural gradients in porous media. Invoking the LEA greatly simplifies the mathematical description and numerical modeling task. Thus, the LEA is often invoked *a priori* since to assume otherwise (non-equilibrium or kinetic processes) usually requires more data and process description than are available. Numerical modeling predictions for remediation based on the local equilibrium presumption have tended to underestimate cleanup times.

Ideal and nonideal sorption

The simplest sorption models assume ideal behavior, which requires local equilibrium, a linear relation between sorbed concentration, S_i, and aqueous concentration, C_i, and a completely reversible sorption reaction without hysteresis. These assumptions are required for application of the familiar retardation factor form of the advection-dispersion Equation 5-1:

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$$R \frac{\partial C_i}{\partial t} = D_x \frac{\partial^2 C_i}{\partial x^2} - v \frac{\partial C_i}{\partial x} \qquad (5\text{-}2)$$

where $R = (1 + \rho_b K_p/\theta)$ with ρ_b as soil bulk density, K_p as the solid/water partitioning coefficient, and θ as the water content. This expression will be examined more closely in Section 5.2.

Evidence of nonideal behavior and the inadequacy of Equation 5-2 is abundant from both laboratory and field-scale experiments. Numerous conceptual and mathematical models to account for the nonideality are reviewed here. Several recent reviews of sorption nonideality are available (e.g., Brusseau and Rao 1989a, Selim, Davidson, and Iskandar 1990, Sawhney and Brown 1989).

Brusseau and Rao (1989a) identify four, potential sources of nonideal sorptive behavior:

a. Isotherm nonlinearity.

b. Sorption—desorption nonsingularity (or hysteresis).

c. Rate-limited or kinetic sorption reactions.

d. Diffusive mass transfer into immobile water regions (e.g., aggregates).

Each of these potential sources of nonideal behavior are reviewed here. Isotherm nonlinearity, sorption kinetics, and hysteresis are chemical phenomena, i.e., they involve specific interactions between the solute and the solids (Sections 5.2, 5.3, and 5.4). Nonideality arising from diffusive mass exchange is a physical nonequilibrium issue (Section 5.5).

Sorption processes are determined to be reversible or irreversible based on observations of tandem adsorption and desorption behavior. If most of the solute mass adsorbed during a controlled adsorption experiment is recovered during desorption (e.g., by sequential, batch extractions with clean water), the process is considered reversible within the time frame of the experiment. If desorption isotherms deviate significantly from adsorption isotherms, the process is hysteretic. If some fraction of the adsorbed mass is not desorbed upon extraction, the process is hysteretic and may be partially irreversible.

Sorbent concentrations in most sorption isotherm experiments are calculated by difference. Implicit in this approach are the following assumptions:

a. All mass "lost" from aqueous solution during the course of the experiment is adsorbed.

b. The sorbate/solute is nonreactive, i.e., not involved in biotic or abiotic reactions.

c. The sorbate/solute is not lost via other modes of interphase exchange, e.g., precipitation, volatilization.

d. The mass of the adsorbents does not change because of dissolution, and solids accretion due to adsorption is negligible.

For XAC solutes, any of these assumptions conceivably may be violated.

Nonequilibrium transport behavior is attributable to either chemical or physical processes, or a combination. Chemical nonequilibrium may be important when adsorption or desorption kinetics are slow relative to advective-dispersive transport or when other unsteady, biogeochemical reactions are active. Physical or diffusion-controlled nonequilibrium is the result of slow diffusive exchange between relatively high advection regions and regions of low or negligible advection. Low mobility or immobile water regions exist at all scales in natural porous media, including intraparticle micropores, intra-aggregate porosity in soils, matrix blocks in fractured porous media, or very fine-grained beds or lenses within aquifer systems.

The influence of nonequilibrium processes on contaminant transport, particularly at the field scale, is not well understood at present. Interest in improving this situation is fueled in part by the growing body of evidence that rate-limited, mass transfer processes impede remediation operations such as pump-and-treat. Equilibrium conditions may be approached locally after extended contact (months to years) between the contaminant and the always heterogeneous medium, assuming the mass flux is near steady-state. However, the LEA becomes a very tenuous assumption wherever conditions are changing rapidly, such as (a) at advancing plume fronts, (b) in association with intrusive remediation technologies, e.g., in situ biotreatment or enhanced solubilization, or (c) in strongly heterogeneous, porous media. Numerical models based on the LEA may have limited predictive capacity in these intrinsically nonequilibrium situations. However, LEA-based models have been useful in modeling many solute transport problems, such as in risk analyses and plume capture modeling.

Partitioning mechanisms

An accurate characterization of the dominant sorption mechanisms is the key to the successful numerical simulation of XAC transport and remediation. Sorption in natural systems always involves interactions between three constituent groups: solutes, solvents, and sorbents. Most sorption process descriptors model interactions of a single solute in a simple aqueous system under well-controlled conditions (e.g., isothermal). However, most contaminated sites involve multiple contaminants and a complex sorbent system such as a soil.

The partitioning mechanism of solutes among the aqueous and solid phases typically is conceptualized as being either a specific "reaction" at a finite number of sites at the sorbent surface or a nonspecific association. Nonspecific sorption mechanisms involve weak solute-sorbent attractive forces and, in the case of highly hydrophobic compounds, strong solvent-solvent interactions that force the solute out of solution (solvophobic partitioning or physisorption). These weak sorptive mechanisms usually are readily reversible. The specific reactions include a variety of sorption mechanisms including ion exchange, surface complexation, hydrogen-bonding, and chemisorption, in approximate increasing order of binding strength and sorption irreversibility. These mechanisms are fundamentally different and process descriptors must reflect this difference. Each mechanism is reviewed below with respect to its relevance or potential relevance to XAC transport (see summary in Table 5.1).

The term sorption "site" is defined in many different ways, depending on the sorption phenomenon of interest. For example, "sites" may refer to the following (Brusseau and Rao 1989a):

a. Specific points on/in the sorbent's molecular framework, e.g., site of charge deficiency or reactive function group.

b. Sorption kinetics type(s), e.g., equilibrium versus rate-limited.

c. Nature of sorbent(s), e.g., soil organics, metal oxyhydroxides, clays.

d. Site accessibility, e.g., surface versus internal to particle or aggregate.

Any particular sorbate-sorbent interaction may be characterized by more than one of these concepts. Atomic substitutions in the crystalline framework (solid solutions) or broken bonds at crystal edges can create charge imbalances, which must be neutralized. Sorption of counterions is a mechanism to maintain electroneutrality (Stumm and Morgan 1981). If there is a traditional conceptualization of a site, it would be the charge imbalance model, particularly in relation to ionic solute sorption. Another form of specific interaction may arise from surface complex formation between functional group substituents of sorbents, particularly polymeric organics, and solute substituents. Several models define sorption sites based solely upon sorption rates. Single and mixed kinetics models have been proposed (e.g., the two-site model described in Section 5.4). Natural soil and aquifer materials are complex mixtures of sorbents, which will possess a unique capacity, strength of bonding, etc., for a given solute. Even a single class of sorbent, such as "soil organic carbon" (e.g., humics), is actually a complex mixture of organic polymers with a variety of functional moieties affecting the net geochemical behavior. Classification of sites based on accessibility to advective flow—sites within high advection (permeable) zones versus sites within aggregate matrices or intragranular micropores—represents one promising approach to dealing with the intrinsically heterogeneous nature of subsurface media.

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Table 5.1
Summary of Adsorption Mechanisms and Their Likely Relevance to XAC Adsorption in Natural Soils and Aquifers[1]

Mechanism[1]	Relevance to XAC Sorption[2]
Nonspecific Interactions	
Hydrophobic partitioning or expulsion	Medium (to High): Low solubilities of nonionic solids, e.g., RDX and HMX.
Partitioning to organic phase (solids or NAPL)	Medium (to High): Mixed indications; weak but positive correlations with bulk f_{oc}; Potential specific interactions with soil organics complicates resolution of simple partitioning.
Specific Interactions	
Induced dipole-dipole interactions	High: Due to electronegativity of nitro groups and molecular polarity; this weak mechanism is almost always active.
Ion exchange	Medium (to Low): Competitive sorption between XACs and/or "implicit" sorbates is speculative. High for ionizable XACs, e.g., amino compounds at $ZPC < pH < pK_a$.
Hydrogen bonding - "water bridge" with Me^{m+} hydration - directly to surface moieties	High (to Medium): Strong indication in nitroaromatics.
Surface complexation	Medium (to High): Between amino or nitro groups and certain organic polymer moieties.
Chemisorption - surface hydrolysis - covalent bonding	High (to Medium): Indications of irreversible sorption and surface catalysis, particularly for TNT compounds.
[1] Few of these mechanisms are documented unequivocally for XACs. [2] The relative significance of each sorption mechanism is ranked qualitatively as High (supportive evidence), Medium (intuition, equivocal evidence, or by analogy to similar compounds), or Low (counter evidence).	

Sorbate molecules must contact sorbent sites in order for adsorption to occur. This obvious and apparently simple requirement is in fact complicated by the presence of a hydrodynamic, surface boundary layer at any solid-liquid interface. Grain coatings of organic or inorganic material, extremely common on soil and aquifer solids, add another layer of complexity to site definition and accessibility. The sorbate molecules can traverse these films by molecular diffusion. If the solute is polar or polarizable, traversing the hydrodynamic layer may be accelerated with electric attractive forces (e.g., van der Waals) between the solute and solid surface. Sorption sites may exist at the coating

surface, in the grain coating, at the grain surface, and/or within the porous grain or aggregate. Intragranular or intra-aggregate sites are accessed by molecular diffusion through the pore or micropore space. The significance of these diffusive processes relative to other XAC transport and remediation processes depends on the scale of observation.

Adsorption is generally an exothermic reaction, i.e., excess free energy is released as heat. Conversely, desorption is typically endothermic. The intensity of exothermy provides an indicator of the strength of the sorbate—sorbent association.

Hydrophobic partitioning or physisorption

Nonspecific adsorption results from either simple partitioning of the solute out of solution and/or weak electrostatic interactions between solute molecules and sorbent sites. The van der Waals forces have low energies of interaction (on the order of 10-40 $kJ \cdot mol^{-1}$) and are effective over short ranges, decreasing rapidly with separation distance (Stumm and Morgan 1981, p 602). These attractive forces are active for all sorbent-sorbate interactions, even if other mechanisms are also active. The van der Waals forces originate from subatomic charge oscillations that induce synchronized dipoles which then attract (Stumm and Morgan 1981).

Nonpolar, hydrophobic organic compounds (HOCs) in dilute, aqueous solution tend to partition into similarly hydrophobic phases, such as organic carbon solids (e.g., soil humics, organic colloids) or organic liquids (e.g., NAPLs or micelles). This partitioning mechanism has little to do with charge imbalances at specific sorption sites. The process is largely one of solute expulsion due to a stronger tendency toward self-association of water molecules by hydrogen bonding than for complexation with nonpolar, organic compounds.

Physisorption models are usually based on the premise that HOC partitioning is independent of solute concentrations below saturation, and is ideal (i.e., negligible sorbate-sorbate, solute-solute, or solvent-sorbent interactions). Since hydrophobic partitioning involves two fairly rapid processes, weak physical adsorption and interphase partitioning (Brusseau and Rao 1989a), equilibrium models are typically invoked. This partitioning mechanism manifests itself in a linear isotherm (Section 5.2) over a wide range of concentration below the compound's solubility limit. Chiou, Peters, and Freed (1979) and many others have suggested that soil organic matter so dominates the sorption of nonpolar, hydrophobic solutes that the process may be treated as a partitioning or dissolution rather than an adsorption reaction, and the specific composition of the soil organics is not critical.

Most crystalline, explosive compounds are sparingly soluble in water, and form nonionic solutes of low to moderate polarity (see Chapters 2 and 4). Hydrophobic partitioning concepts and the role of soil organics will be

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revisited in reference to linear isotherms (Section 5.2), enhanced sorption and desorption (Section 5.9), and nonequilibrium models explicitly involving diffusive exchange with organic matter (Section 5.5).

Hydrogen-bonding, ion exchange, and chemisorption

Specific interactions between solute molecules and sorbents tend to be more energetic than physisorption interactions. Nitroaromatics and nitrogen heterocyclics have potential for hydrogen bonding and dipole-dipole interactions due to the polarity of aromatic nitro and amino groups.

Hydrogen bonding. Hydrogen bonding is an interaction between polar molecules involving a partial charge transfer (Figure 5.1). Hydrogen bonds (HBs) show approximately the same to a slightly greater energy range as van der Waals interactions—10 to 40 kJ mol^{-1} (Stumm and Morgan 1981). HBs can form between molecules of solvent (e.g., water-water), solute, or solute-sorbent (e.g., surface hydroxyl or adsorbed water). Since partial charge transfer may occur, this bond involves a Lewis acid (electron pair acceptor) and base (electron pair donor).
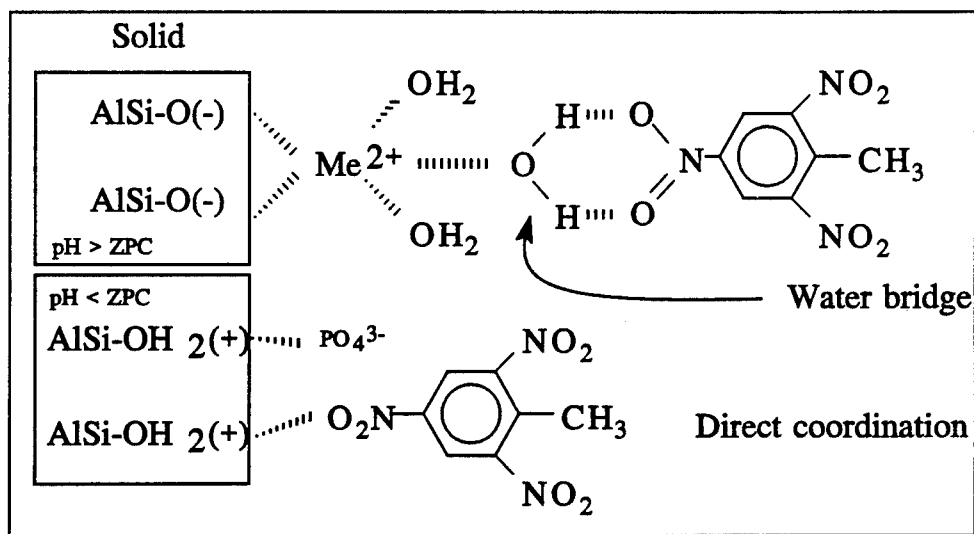
Figure 5.1. Schematic of TNT hydrogen-bonding mechanisms through a cation—"water-bridge" (top), and direct nitro-hydroxyl coordination (bottom)

Several investigators have suggested hydrogen bonding as a possible mechanism for observed associations between amino- and nitro-functional groups and various sorbents. HBs may develop between the surface Si-O or -OH groups of phyllosilicate minerals (Stumm and Morgan 1981) and the R-NH group of alkylammonium ions (Johns and Sen Gupta 1967) or aliphatic amines (MacEwan and Wilson 1980, Brindley 1965).

The primary hydration shell of metal cation sorbates (Me^{2+} in Figure 5.1) may act as a "water-bridge" between a polar organic solute and sorption sites

on clay mineral or solid humic sorbents (Morrill, Mahilum, and Mohiuddin 1982, Yariv, Heller, and Kaufher 1979). This bridging mechanism has been suggested for associations between smectite ((expandable, high-cation exchange capacity (CEC), clay minerals)) and nitrobenzene (Parfitt 1969), amide (Tahoun and Mortland 1966), TNT (Leggett 1985, 1991), and other natural organics such as humic and fulvic acids (Morrill, Mahilum, and Mohiuddin 1982).

Hydrogen bonds may be involved in the sorption of dissolved humic matter to inorganic sorbents via attraction of the humic carbonyl bond (C $=$ O) and the surface hydrogens. Other functional groups on the humic sorbate may in turn be sorption sites for other organic solutes or bridging atoms/molecules. Hydrogen bonding appears to play a significant role in the formation of relatively stable complexes of large or polymeric, organic molecules, which could affect XAC enhanced sorption (immobile complex) or solubilization (for mobile complex).

Ionic bonding and ion-exchange. Electrical interactions between solute and sorbent may be broadly categorized as either electrostatic or polarizing. Electrostatic interactions involve two or more entities of opposite and permanent charge, e.g., sorption of metal cations (Me^{+m}) to a negatively charged clay surface. Polarizing interactions involve the mutual induction or enhancement of the individual dipole(s). At least one of the participants is polar (dipole-dipole interaction) or ionic (ion-dipole interaction). This electrochemical sorption mechanism is the product of the natural tendency toward electroneutrality, ionic solutes serving as counterions to satisfy charge imbalances in/on the solid.

Most common soil mineral surfaces are negatively charged at circumneutral, environmental pH's. Cationic or polar nonionic solutes may show an affinity for specific sites of charge deficiency and/or specific surface functional groups. The energies of interaction between each sorbate and sorbent site type vary, resulting in certain interactions being favored over others. This competition for a particular class of sorption sites will be influenced by the aqueous system chemistry, i.e., sorption is influenced by solute concentrations, speciation, pH, Eh, temperature, etc. Sorbent heterogeneity further complicates the modeling task. Unfortunately, the quantitative effects of these variables on XAC sorption is unknown.

Counterions must occupy charge-deficient sorption sites at all times to maintain electroneutrality. Prior to the introduction of contaminant ions (e.g., Me^{2+}, NH_4^+, $Ar-NH_3^+$), the counterions are likely to be common, natural ions or ionic complexes (e.g., H^+, Na^+, K^+, Ca^{2+}, or Fe^{2+}). If the sorbent has a strong affinity for the contaminant, the initial counterion is displaced readily, and its effect on contaminant sorption and rates may be negligible. Conversely, if the sorbent shows a strong selectivity for the initial counterion, the contaminant ion is not retarded by those sites occupied by the preferred counterion. Between these extremes, initial and contaminant ions compete for available sites. The extreme cases are relatively easy to model as they are

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more likely to conform to traditional, single component, sorption models. The intermediate case is much more complicated, requiring the description of variable sorbent selectivity, sorption kinetics, and transport equations for multiple constituents, i.e., an ion exchange model. Descriptors for multiple sites and competitive sorption are discussed in Section 5.2.

Since the ubiquitous, hydronium cations (H_3O^+ or H^+) compete with ionic or strongly polar organic species for sorption sites, partitioning would be expected to be pH dependent if this competitive sorption mechanism is active. The pH is a primary influence on the net surface charge of a solid (Stumm and Morgan 1981). At high pH's (low H^+ concentration), the negative surface charge will tend to be balanced by other counterions. At a critical pH, the H^+ concentration will be sufficient to exactly satisfy the charge imbalance; this is the sorbent's zero point of charge (ZPC). At pHs below the ZPC, an excess of H^+ creates a positively charged surface, which, of course, can dramatically affect the sorption of other charged species. Pennington and Patrick (1990) reported no significant or consistent trends in the effect of pH (5, 6.5, and 8) on TNT sorption under reducing (Eh = -150 mV) or oxidizing (Eh = +450 mV) conditions for a soil from the Joliet Army Ammunition Plant (f_{oc} = 0.036). However, the sorbents are not sufficiently characterized to dismiss pH effects at more extreme pHs (soil pH can be much lower than 5).

Organic solutes may exert some influence on the sorption behavior of other solutes present, though this possibility is usually neglected by assuming ideal behavior (negligible solute-solute interactions) in dilute solution. This cosolvency effect is discussed in Section 5.9. The possibility of synergistic sorbate-sorbate interaction also exists; for example, uptake of one organic into expandable clay interlamellae may enhance the uptake of a second organic (MacEwan and Wilson 1980).

XAC coordination and ion exchange. Amino functional groups (Ar-NH$_2$) can protonate to ammonium groups (Ar$-$NH$_3^+$) at pH's below their acid association constant, pK$_a$ (see Stumm and Morgan (1981) for a discussion of pK$_a$'s; also Section 8.3). Though pK$_a$'s for nitroaromatics are usually fairly low (e.g., the pK$_a$ for aniline is 4.6 (Theng 1974); also see Figure 7.1), low pHs are not uncommon in soils. Numerous soil minerals have ZPCs below 4, e.g., montmorillonite (2.5), Sio$_2$ (2.0), and feldspars (2-2.4) (Stumm and Morgan, 1981).

Adsorbed and solute cations develop coordination complexes or sheaths consisting of water, polar, or counterionic solutes. An adsorbed cation can affect the sorption of polar aromatics in at least two ways: (a) hydrogen bonding through coordinated water molecules as discussed above, or (b) direct bonding between the cation and the aromatic ring electrons (Mortland 1970, MacEwan and Wilson 1980). The relevance of these mechanisms for XAC sorption should be investigated. A positive correlation between TNT sorption and soil, extractable Fe is evident (Ainsworth et al. 1993, Pennington and Patrick 1990); soil iron compounds, perhaps as amorphous FeOOH, may be

acting as direct or coordination binding sites. Metal cations vary with respect to solvation energy and the intensity of their retention of their primary hydration shell, e.g., $Mg^{2+} > Fe^{2+} > Pb^{2+}$ (MacEwan and Wilson 1980). Increased XAC sorption correlated to ion hydration intensity would be consistent with the water bridge mechanism.

The formation of complexes between transition metal ions and aromatic compounds by donating π-electrons to the aromatic ring has been reported for benzene, toluene, and others (Doner and Mortland 1969, MacEwan and Wilson 1980). This mechanism likely would be more important in nitroaromatics due to the electron-drawing effects of the nitro groups.

Leggett (1985, 1991) suggests that nitroaromatics can be either electron donors or acceptors in hydrogen bonding to soils by either direct coordination to surface hydroxyls or through the coordinated water bridge mechanism, as shown in Figure 5.1. Hydroxyl groups are common on the surfaces of silicate and oxyhydroxide minerals and organic polymer (Stumm and Morgan 1981, Sposito 1986).

A general ion exchange reaction for solute N^{n+} displacing sorbate M^{m+} from the cation exchange site $[S^{(-)}]$ may be represented as:

$$[S^{(-)}]_{solid} \, n[M^{m+}] + m \, N^{n+} \rightleftharpoons [S_{(-)}]_{solid} \, m[N^{n+}] + n \, M^{m+} \qquad (5\text{-}3)$$
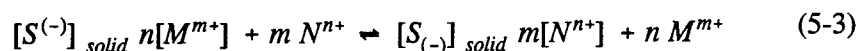
where the brackets indicate sorbent/sorbate. The relative affinity of the solid for ions M^{+m} and N^{+n} may be described in terms of the selectivity coefficient (K_s):

$$K_s = \frac{X_{SN}^m \, [M^m]^n}{X_{SM}^n \, [N^n]^m} \qquad (5\text{-}4)$$

where X_{Si} (i $= M$ or N) indicates the fraction of ionic species i sorbed (in equivalents). However, selectivity coefficients should be considered as semi-quantitative, mass-law descriptors of equilibria because they are thermodynamically ill-defined, empirical parameters and not constant (Stumm and Morgan 1981, p 643-44).

Several interface-scale conceptual models have been proposed to describe sorption and ion exchange (Stumm and Morgan 1981). These models conceptualize the sorbent-solution interface as a multilayer electrostatic system (e.g., Stern layer, Gouy-Chapman layers, triple-layer models). This scale of modeling is difficult to verify and impractical for engineering application. All of the existing ion-exchange models are at least partly empirical, and none are sufficiently general for universal application (Johnson, Palmer, and Fish 1989). Process descriptors for these molecular-scale ion exchange models are not reviewed here.

An innovative, in situ, plume management technology in which cation adsorption plays a crucial role involves the emplacement of a subsurface sorption system (SSS)—a cationic surfactant (e.g., hexadecyl-trimethylammonium chloride) barrier intended to retard the advance of hydrophobic organic compounds (HOCs) in low organic carbon aquifers (Hatfield et al. 1992, Brown et al. 1992). The cationic portion of the surfactant would bind to the exchange sites, while the aliphatic portion would mimic the behavior of the natural organic solids, into which HOCs would partition. A modified version of this sorption fence technology could be applied to XAC plumes.

Cation exchange capacity. Most natural, inorganic, soil solids are cationic exchange bases, i.e., their surface is negatively charged at circumneutral pH's. The cation exchange capacity (CEC) is a measure (milliequivalents per gram solid) of the sorbent's capacity to remove cations from solution and an indicator of the charge imbalance in the sorbent material. The CEC is a fundamental determination in the characterization of a soil or aquifer material, particularly when transport of ionic or polar solutes is of concern.

Pennington and Patrick (1990) reported a significant, positive correlation ($r^2 = 0.76$) between the CEC and TNT adsorption, as represented by a single K_d value (though best-fit isotherms were slightly nonlinear). Correlation between K_d and extractable iron was also moderate ($r^2 = 0.79$), while much weaker correlations were reported for percent clay ($r^2 = 0.49$) and organic carbon ($r^2 = 0.16$). These characteristics (iron, CEC, organics, clays) are not entirely independent, but the positive correlations with K_d suggests that some manner of specific interaction mechanism is active.

With a few exceptions, XACs are hydrophobic, nonionic, and of low to moderate polarity. Some XACs, however, are ionic (e.g., ammonium picrate) or ionizable at low pH (e.g., any aminodinitrotoluene). Indications that ion exchange (or chemisorption) may be important in the transport of XACs highlight the need for complete characterization of the soil composition, particularly organic carbon constituents, oxyhydroxides, mineralogy, and other components that potentially affect electrical interactions.

Chemisorption. Chemisorption is a class of exothermic reactions between solutes and specific sorbent sites, involving the redistribution of electrons and the potential formation of covalent bonds (Morrill, Mahilum, and Mohiuddin 1982). Covalent binding energies are much greater (≈ 40 kJ mol^{-1}) than van der Waals forces (Stumm and Morgan 1981).

Chemisorption is not necessarily irreversible, though this mechanism likely contributes to the partial irreversibility observed for many nitro- an amino-organic solutes onto clay or organic sorbents (Parris 1980, Hsu and Bartha 1974). Partially irreversible sorption reactions have been suggested in several cases of XAC sorption (Leggett 1991, Brannon et al. 1992). Leggett (1991) suggests, by analogy to sorption reactions of other nitro- and amino-aromatics with soil organics, that XACs can be either electron acceptors or donors in

interactions with various functional groups (particularly hydroquinones) in soil organics. These reactions can result in the reduction of nitro groups and irreversible coupling of amino-XACs with soil organics. Trinitrobenzene has been described as the "quintessential electron-pair acceptor" in charge transfer reactions.

Irreversible reactions are relatively easy to describe mathematically in terms of reaction rate kinetics. However, the mechanism must be well understood to be of much practical use in preparing mass balance equations. Rate-limiting controls must be established and methods developed to quantitate those controls in natural, heterogeneous soil systems. As with ion exchange, competition for chemisorption (reaction) sites may be important for some solutes, and selectivity is likely to be more severe due to thermodynamic or kinetic constraints. The finite capacity of such strongly binding sites would be consistent with a Langmuir sorption model (Section 5.2).

The apparent irreversibility of a sorption reaction does not require a chemisorption process. The frequently reported observation of increased irreversibility with longer contact times between solute and soil may be indicative of either another sort of reaction (e.g., catalysis), or may reflect a diffusion limited release of the solute from the interstices of soil grains or clay interlamellae.

5.2 Equilibrium Models

Equilibrium sorption models describe the dependence of sorbate concentration (S_i) upon the equilibrated aqueous solute concentration (C_i) typically with a simple algebraic expression. Sorption isotherm expressions take many forms (see Table 5.2), though only a few are commonly utilized in general practice. Utilization of isotherm expressions in transport modeling involves several implicit assumptions:

a. Constant temperature.

b. Singularity or reversibility.

c. Nonreactive sorbent.

The model parameters strictly apply only at the temperature (and other conditions) under which experiment data were collected. Singularity requires that the desorption isotherm be the same as for adsorption; nonsingularity suggests that some other process is active. If the reaction is reversible but nonsingular, then "isotherm" expressions (strictly, no longer an isotherm) would be unique for each desorption and readsorption pathway, requiring an extraordinary level of effort to characterize. To be reversible there must not be any significant

Table 5.2
Summary of Representative Adsorption Isotherm Models[1]

Isotherm	Equation[2]	Number of Adjustable Parameters	Asymptotic Properties	
			Linear at Low C	Sorption Maximum
Linear (Lin)	$S = K_d C$	1	yes	no
Langmuir (L)	$S = \dfrac{K_L S_{max} C}{1 + K_L C}$	2	yes	S_{max}
Multisite Langmuir (MSL)	$S = \sum_{n=1}^{N} \dfrac{K_{L(n)} S_{max(n)} C}{1 + K_{L(n)} C}$	2N	yes	$\Sigma\, S_{max}$
Competitive Langmuir (CL)	$S_j = \dfrac{K_{L(j)} S_{max(j)} C_j}{1 + \sum_{j=1}^{k} K_{L(j)} C_j}$	2j	yes	S_{max} $(C_{j=1\rightarrow k})$
Freundlich (F)	$S = K_F C^{b_F}$	2	no[3]	no
Sum of Freundlichs (SF)	$S = \sum_{n=1}^{N} \left(K_{F(n)} C\right)^{b_{F(n)}}$	2k	no	no
Exponential RJ[4]	$S = K_1 C\, e^{-2K_2 S}$	2 (K1, K2)	no	no
Scatchard	$\dfrac{S}{C} = K(m - S)$	2	var.	var.; yes, if m = S_{max}
Langmuir-Freundlich (LF)	$S = \dfrac{(K C)^{\beta} S_{max}}{1 + (K C)^{\beta}}$	3	no	S_{max}
Redlich-Peterson (RP)	$S = \dfrac{K C\, S_{max}}{1 + (K C)^{\beta}}$	3	yes	no
Tóth	$S = \dfrac{K C\, S_{max}}{\left[1 + (K C)^{\beta}\right]\frac{1}{\beta}}$	3	yes	S_{max}
Modified Kjelland (MK)[4]	$S = \dfrac{C\, S_{max}}{C + k_1\,(C_m - C)\, \exp\!\left[k_2\,(C_m - 2C)\right]}$	3	yes	S_{max}
Dubinin - Radushkevich	$\log S = -\beta\left[\log^2(K C)\right] + \log S_{max}$	3	no	no
Modified Dubinin - Radushkevich (MDR)	$\log S =$ $\lceil \log n* - \log c* + \log C \quad c \le c*$ $\lfloor -\beta\left[\log^2\dfrac{KC}{1+KC}\right] + \log S_{max} \quad c \ge c*$	3	yes	S_{max}
General Polynomial	$S = \sum_{i=1}^{N} a_i C^i$	N	var.	var.

[1] Modified and supplemented from Kinniburgh (1986).
[2] S = sorbate concentration; C = solute concentration; C_m = maximum aqueous concentration; K_d = linear partition coefficient; K_F, b_F = Freundlich coefficients; S_{max} = maximum sorbate concentration; K_L, b_L = Langmuir coefficients; β = heterogeneity factor; var. = may observe asymptotes, depending on parameter values; (c*, n*) = point where $(\partial \log n)/(\partial \log C) = 1$.
[3] Becomes linear for $b_F = 1$.
[4] Rao and Jessup (1982).

chemical reactions (e.g., covalent bonding, reduction) between the sorbate and sorbent. Violations of these assumptions are quite common, but the net effect on solute transport may be sufficiently small to justify making the simplifying assumptions.

Most adsorption isotherm models assume a monotonic sorption relation, i.e., partitioning either increases or decreases with equilibrium solute concentration. Violation of this trend suggests a mechanism other than sorption (e.g., aqueous complexation or micelle formation) is involved in addition to adsorption.

The simplicity of equilibrium sorption descriptors in the advection-dispersion Equations 5-1, 5-2 is attractive for both conceptual and numerical modeling. The conditions under which the LEA is valid depends on the relation between the rates of flow and geochemical processes. The Damkölher numbers (ω_I, ω_{II}) are dimensionless parameters expressing the significance of reactions (in the most general sense) relative to transport:

$$\omega_I = \frac{k\,L}{v} \qquad\qquad I$$

$$\omega_{II} = \frac{k\,L^2}{D} \qquad\qquad II$$

(5-5)

where k [T^{-1}] is the process rate constant (e.g., mass transfer coefficient), L is the system length, and D is the dispersion coefficient [L$^2\cdot$T^{-1}]. The first Damkölher number (ω_I) is applicable at high Peclet numbers (Pe $= vL\,/\,D$); the second Damkölher number (ω_{II}) is useful at lower Peclet numbers (Dominico and Schwartz 1990). Relating LEA indicators to a particular system requires careful analysis. Several quantitative assessments of the validity range of the LEA have been proposed for various systems (Valocchi 1985, Parker and Valocchi 1986, Bahr and Rubin 1987, Brusseau and Rao 1989a, Harmon, Ball, and Roberts 1989). In the final analysis, the choice to accept the LEA or choose a kinetic model is a practical one for which the investigators use their judgment.

Linear isotherm

Retardation factor. For many sorbate-sorbent interactions, particularly for low concentrations (C_i) of sparingly soluble, low-polarity organics, the adsorbed concentration (S_i) may vary linearly with the aqueous concentration:

$$S_i = K_{d\,(i)}\, C_i$$

(5-6)

where $K_{d(i)}$ is the distribution coefficient for solute i [L$^3\cdot$M$_s^{-1}$ $=$ M$_i\cdot$M$_s^{-1}$ / M$_i\cdot$L^{-3}]. Taking the $\partial/\partial t$ of Equation 5-6, substitution into Equation 5-1 and rearrangement yield (dropping the constituent subscript i):

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$$\frac{\partial C}{\partial t} = \frac{1}{R} \left[D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \right] \qquad (5\text{-}7)$$

where R is the retardation factor defined as:

$$R \equiv 1 + \frac{\rho_b}{n_e} K_d \qquad (5\text{-}8)$$

The effect of R is to impede or retard solute transport relative to advective-dispersive transport. Implicit in the application of this form of the retardation factor are the assumptions of constant temperature (isothermal), linear equilibrium partitioning, and reversible sorption.

Range of linearity. The conceptual and mathematical simplicity of the linear isotherm is appealing, which certainly contributes to its being the most commonly used model. Linear relations are much more amenable to analytical, mathematical solutions. Accommodation of nonlinear isotherm models into transport codes is somewhat more complex, requiring some form of numerical solution. Several researchers have offered general rules-of-thumb as to the conditions for which linear behavior may be reasonably expected, at least for nonpolar, hydrophobic organics.

Linear partitioning may be an adequate sorption model for many nonpolar, hydrophobic organic solutes. Chiou, Peters, and Freed (1979) examined sorption of nonpolar, hydrophobic, chlorinated solvents (also PCBs and pesticides) onto soil organic carbon. Linearity is observed as high as 0.95 times the solubility limit. Karickhoff, Brown, and Scott (1979) offers as a guideline that linear isotherms can be expected if the observed/anticipated aqueous concentrations are below 10^{-5} M ((10^{-3} M in Karickhoff (1981)) and half the solutes' solubility.

Munz and Roberts (1986) examined the effect of concentration and the presence of cosolvents on the activity coefficient at infinite dilution (γ^{∞}) for several chlorinated solvents. They observed that γ^{∞} is independent of concentration below the 10^{-3} mole fraction level (or 0.056 M). With a few exceptions (e.g., picric acid), the common explosives have aqueous solubilities of less than 0.002 M (see Table 4.1), suggesting that near-linear isotherms should be anticipated. More polar or ionizable organics (e.g., amino-compounds) tend to demonstrate nonlinear sorption, even at low concentrations, perhaps reflecting more complex sorption mechanisms such as surface complexation. Even if the full isotherm is nonlinear, portions of the isotherm often can be approximated as linear (a piecewise linear approach).

Unfortunately, K_d values are highly system-specific, varying with the method of determination, environmental conditions, and geochemistry of both the aqueous and solid phases (Dominico and Schwartz 1990). Laboratory determined values (isotherms) often are not consistent with field-based

estimates (by inverse modeling), indicative of the problem in collecting representative samples and in scaling bench observations to the field. Application of parameters to field cases other than that for which the parameters were determined should be regarded as extremely tenuous.

Fraction organic carbon models. The high sorptive capacity of soil organic carbon so dominates the partitioning of nonpolar HOCs that descriptors based solely on soil organic carbon partitioning have been proposed and applied with reasonable success as an initial approximation. A linear partitioning coefficient (K_d; mass adsorbed per equilibrated aqueous concentration) may be defined alternatively in terms of an organic carbon partitioning coefficient (K_{oc}):

$$K_d = K_{oc} f_{oc} \qquad (5-9)$$

where f_{oc} is the mass-fraction of organic carbon in the soil (Chiou, Peters, and Freed 1979, Karickhoff, Brown, and Scott 1979, Chiou 1989).

Significant retardation of HOC transport is generally observed when solid, organic carbon fraction (f_{oc}) in the soil or aquifer material exceeds 0.001 (Karickhoff, Brown, and Scott 1979, Schwarzenbach and Westall 1981, Brusseau and Rao 1989a). The consensus appears to be that as long as retention of nonpolar HOCs is dominated by soil organic carbon material that the contribution of other sorbents to HOC retardation is relatively much less significant and may be neglected, at least initially. However, at f_{oc}s near or below 0.001 the K_d - f_{oc} correlation breaks down as other retarding processes become more conspicuous, such as sorption onto tectosilicates, clay minerals, and metal oxyhydroxides. Low f_{oc} is common in sand and gravel aquifers. Barber, Thurman, and Runnells (1992), for example, suggest that magnetic minerals (e.g., ilmenite, magnetite) may become significant sorbents of chlorobenzenes in a low carbon aquifer in Cape Cod, MA.

Numerous, empirical, linear relations have been advanced to assess relations between the organic carbon/water partitioning coefficient (K_{oc}) and the octanol/water (K_{ow}), which in turn is correlated to aqueous solubility (see Appendix B). Such correlations provide a tool with which to estimate the behavior of incompletely characterized compounds based on the behavior of similar compounds.

The octanol-water partitioning coefficient, K_{ow}, is a standard indicator of how a chemical partitions between the aqueous phase and an organic phase, octanol serving a surrogate for fat and other biological tissues, soil organic carbon, or organic immiscible liquids (OILs).

K_{oc}-K_{ow}-S relations generally are developed for a suite of similar, nonpolar, hydrophobic organic compounds, predominantly saturated aromatics (e.g, PAHs) and aliphatics (e.g., petroleum hydrocarbons) with methyl functional groups, or chlorinated organics (e.g., TCE pesticides). Extension of these

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correlations to other compounds (e.g., nitroaromatic explosives) must be done with caution and with the realization that the estimate may be only within an order of magnitude. K_{oc}-K_{ow}-S correlations exclusively for nitroaromatics or nitrogen heterocyclics are not available and should be established. It may be that such relations for polar organics show too strong a dependence on the nature of the sorbent (not the case for nonpolar HOCs) to yield useful correlations.

Banerjee, Yalkowsky, and Valvani (1980) evaluated the relation ($r^2 = 0.96$) between aqueous solubility (S_w) and K_{ow} for 27 compounds (mostly chlorinated aromatics and aliphatics):

$$\log K_{ow} = 6.5 - 0.89 \log S_w - 0.015 \, MP \qquad (5\text{-}10)$$

where MP is the melting point (°C). They demonstrate that a correction is required for high melting point compounds, such as RDX, to permit inclusion of both solid and liquid compounds in the same correlation.

Solubility and K_{ow} data are available for many compounds, including explosives (e.g., Rosenblatt et al. 1989; see Appendix A), and the organic carbon fraction is now a fairly standard analysis in soil characterization. So a $K_{d(oc)}$ value is easily estimated, at least for soils and aquifer material with significant amounts of organic carbon.

Karickhoff (1984) and Yalkowsky and Banerjee (1992) note that predictions of K_{oc} based on K_{ow} are much more reliable than those based on solubility. The K_{oc} values tend to correlate well with HOC hydrophobicity, more so than does the K_d which is more dependent on the specific sorbate-sorbent pair involved, i.e., K_{oc} is much less variable for a given HOC.

Sorption of HOCs is complicated by association with DOC (dissolved organic carbon) as well as potentially mobile particulate organic carbon (POC) (e.g., organic colloids). Humic and fulvic acids are the dominant DOCs and can exert significant influence on organic solutes with K_{ow}'s greater than 10^4 (Karickhoff, Brown, and Scott 1979).

Nonlinear isotherms

Within the limits of linear sorption behavior, the slope (K_d) of the $\partial S/\partial C$ relation is independent of the aqueous activity (or concentration, fugacity). When $\partial S/\partial C$ varies with the aqueous activity of the solute, the isotherm is nonlinear and $K_d = K_d(C)$. Nonlinearity indicates that a sorption mechanism other than simple hydrophobic partitioning is operative (e.g., specific sorption mechanisms such as chemisorption of ionic or polar solutes, or rate-limited processes). Several nonlinear isotherm models have been proposed (see Table 5.2), but the two most commonly invoked are the Freundlich and Langmuir isotherms.

Freundlich isotherm. The Freundlich model describes the nonlinear sorption relation as an exponential (b_F) function of solute concentration:

$$\frac{dS_i}{dt} = k_{Ads}\, C_i^{b_F} - k_{Des}\, S_i \tag{5-11}$$

where k_{Ads} and k_{Des} are the adsorption and desorption rate constants, respectively. At equilibrium dS/dt is zero, and rearranging Equation 5-11 yields:

$$S_i = \frac{k_{Ads}}{k_{Des}}\, C_i^{b_F} \tag{5-12}$$

Combining the rate constants yields the familiar Freundlich isotherm:

$$S = K_F\, C^{b_F} \tag{5-13}$$

The Freundlich unit-capacity coefficient, K_F, is related to the sorbate capacity for the sorbent. The coefficient b_F is interpreted as a measure of the relative magnitude and diversity of the energies of the sorption process (Miller and Weber 1984, Weber, McGinley, and Katz 1992). The Freundlich model imposes no presumptions of finite sorbent capacity or homogeneity of the site energies, which may be more appropriate for heterogeneous, natural sorbents for which b_F values from 0.4 to over 1.0 are reported (Weber, McGinley, and Katz 1992).

Model parameters are calculated typically by fitting batch adsorption experiment data to a linearized form of Equation 5-13:

$$\ln S = \ln K_F + b_F \ln C \tag{5-14}$$

The fitted parameters may be sensitive to the sorbate concentration range, soil mass, aqueous chemistry, and any imposed ln S intercept (nonzero, zero, or assumed zero), which should be reported along with a correlation coefficient as a quantitative indicator of model goodness of fit. Kinniburgh (1986) suggests that unbiased parameter estimates are more readily obtained by nonlinear regression analysis, which is relatively easily done with the aid of any of several available statistical software packages. Kinniburgh also suggests adding a constant, relative error coefficient when appropriate, to Equation 5-14, in which case Equation 5-13 becomes $S = K_F\, C^{b_F}\, e$. Regression on the linearized form (Equation 5-14 + e) provides reliable Freundlich parameters.

The Freundlich isotherm reduces to a linear function when $b_F = 1$. For $b_F > 1$, a plot of C versus S (dependent variable; ordinate) is a concave

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upward curve. More often, b_F is less than one, in which case the isotherm curve is concave downward. The Freundlich isotherm may appear approximately linear at low aqueous concentrations and asymptotic on some S value (for $b_F < 1$) or C value (for $b_F > 1$) at high concentrations. The extrema of the Freundlich isotherm indicate counter-intuitive, sorption behavior. For example, for $b_F > 1$, sorption is unlimited. For $b_F < 1$, the isotherm slope approaches infinity as C approaches zero, which suggests complete adsorption. These observations indicate potential limitations of applicability, not model invalidity.

Taking the $\partial/\partial t$ of the Freundlich isotherm expression, Equation 5-13, and incorporating into Equation 5-1 yields the somewhat more complicated retardation factor (R_F) (Goode and Konikow 1989; Groves and Stollenwerk 1984):

$$R_F \equiv 1 + \frac{\rho_b}{n_e} K_F\, b_F\, C^{b_F - 1} \qquad (5\text{-}15)$$

For $b_F < 1$, an advancing solute front would be self-sharpening, i.e., maintain a steeper concentration gradient, since the lower concentrations at the leading edge are more effectively sorbed (greater K_d; steeper isotherm slope). As concentration increases behind the front, the solute is less impeded and "catches up" with the leading edge. The trailing edge of a plume (or pulse) has lower concentrations and is adsorbed more effectively again, as was the leading edge, and so creates a lagging tail on the breakthrough curve. The opposite would be true for $b_F > 1$, i.e., the relatively dilute, advancing edge is less impeded and breaks through earlier than the high concentration plume immediately following. The trailing edge is also relatively less impeded, creating a self-shortening tail (less lag).

Langmuir isotherm. This isotherm describes the adsorption process as the reversible formation of a monolayer—an adsorbate layer of finite capacity, perhaps a single molecule thick. Alternatively, sobate molecules are assumed to sorb to a finite population of uniformly distributed sorption sites of uniform energy. Conceptually, once the monolayers (or sorption sites) are filled, subsequent sorption outside the monolayer would be weak and the additional sorbed mass negligible, thus the monolayer capacity represents a critical, if not maximum, adsorbate concentration (S_{max}; $M_i \cdot M_s^{-1}$). The Langmuir isotherm model:

$$S = \frac{K_L\, S_{max}\, C}{1 + K_L\, C} \qquad (5\text{-}16)$$

contains an enthalpy-related parameter K_L [$L^3 \cdot M^{-1}$], interpreted as an indicator of the affinity of the surface for the sorbate. Implicit in the Langmuir model is the presumption of a single and constant site energy, a concept likely to be inappropriate for heterogeneous soil sorbents.

The adsorbate partitioning coefficient (isotherm slope) is a nonlinear function of the amount of S_{max} available. At very low concentrations, such that $K_L C_i < < 1$, the expression is approximately linear (slope $= K_L$). At high concentrations, partitioning ($\partial S / \partial C$) is independent of C, sites are saturated ($S = S_{max}$), and no additional adsorption occurs. The imposition of a limited sorption capacity is consistent with certain sorption mechanisms which are based in electoneutrality (e.g., ion exchange, polar solute complexation) or involve reaction with a finite number of sorbent functional groups (e.g., hydrogen bonding). For hydrophobic partitioning, however, a single-layer, maximum capacity is counterintuitive. The breakthrough curve for a solute characterized by a Langmuir isotherm would be similar to the self-sharpening front and extended post-plume tailing described above for a Freundlich isotherm model with $b_F < 1$ (most common).

Langmuir isotherm parameters are obtained typically by fitting batch, adsorption data to a linearized form of Equation 5-16. Several linearized forms have been proposed (Kinniburgh 1986), such as the popular, double-reciprocal (Lineweaver-Burk) form:

$$\frac{1}{S} = \frac{1}{S_{max}} + \frac{1}{K_L S_{max}} \left[\frac{1}{C} \right]$$

(5-17)

for which $1/S$ versus $1/C$ has an intercept of $1/S_{max}$ and a slope of $1/(K_L S_{max})$, thus $K_L =$ intercept/slope. Kinniburgh (1986) discusses the relative advantages and disadvantages (mostly the latter) of parameter estimation based on weighted and unweighted linear regression on linearized forms. He advocates the use of readily available, nonlinear, least-squares (NLLS) regression techniques to avoid biasing the parameter estimate and to enhance isotherm model generality. Unweighted linear regression using the double-reciprocal equation yields estimates within the range of other estimates (Kinniburgh 1986). The retardation factor form of the Langmuir isotherm (Goode and Konikow 1989, Groves and Stollenwerk 1984) may be expressed as

$$R_F \equiv 1 + (\rho_b / n_e) K_L S_{Max} (1 + K_L C)^{-2} \cdot$$

Other isotherms. The Freundlich and Langmuir models are by far the most widely used nonlinear isotherms. Their popularity may be as much related to their conceptual simplicity and ease of application (e.g., parameter estimates by linear regression) as it is to their theoretical soundness. Although the Freundlich and Langmuir isotherm parameters have some conceptual and thermodynamic basis, such as the monolayer capacity or the enthalpy dependence of the Langmuir K_L, in practice they are empirical parameters. Any of the isotherm expressions can be applied to any data set. Simply fitting an isotherm expression well (e.g., higher r^2 value) does not validate the conceptual model.

Many other isotherm models have been proposed in addition to those listed in Table 5.2. No sorption models are yet sufficiently general to utilize predictively, i.e., all require either calibration against experimental data (all of Table 5.2) or are burdened with too many variables for practical application (e.g., microscale, multilayer interface models).

Multiple equilibria models

Natural soils and aquifer materials are intrinsically heterogeneous in terms of mineralogy and organic sorbent content. One approach to capturing the effects of this chemical heterogeneity on sorption is to represent the multiple sorbents with a finite number of classes. The representative sorbents may be defined specifically or operationally. If soil analyses and an awareness of active sorption mechanisms indicate that sorption is dominated by a few constituents, then sorption models can be based on those specific constituents. If only bulk sorption behavior is known, the more common case, and nonideal behavior is indicated, then a simpler approach is to classify sorbents based on possible substituent behaviors, perhaps based on isotherm form. The isotherms may be any combination of linear and nonlinear models. Interaction between organic solutes and soil humic matter (particulate or dissolved) is an excellent and relevant example for the utility of multiple site modeling because soil organics typically possess a variety of functional groups (or sites).

As long as sorbate-sorbate (or solute-solute) interactions are negligible, multiple sorbates can be modeled independently. If solute-sorbate partitioning is significantly affected by the presence of another constituent, then some form of competitive sorption model is required. Sorption to multiple sorbents likely will require simultaneous solution of isotherm equations.

Kinniburgh (1986) suggests that once liberated from the confines of linear regression, more general isotherm expressions can be utilized which are much more amenable to heterogeneous sorbents and competitive sorption modeling. All of the more general models involve three or more parameters (Table 5.2) and thus greater degrees of freedom. Kinniburgh reviews example applications of the multisite Langmuir, Tóth, and modified Dubinin-Radushkevich isotherms.

Multiple linear isotherm models. Karickhoff, Brown, and Scott (1979) and also Karickhoff (1984) observed that at low concentrations, hydrophobic organic solutes behave ideally and the sorption of a single solute onto multiple (N) sorbents is additive:

$$S = \sum_{n=1}^{N} K_{d(n)} C \qquad (5\text{-}18)$$

If sorption is largely a hydrophobic mechanism and sufficient organic carbon is present, then the bulk partition coefficient (K_p) may be attributed to the sum of partitioning onto M organic sorbent constituents:

$$K_p = \sum_{m=1}^{M} K_{p(m)} \, f_m \, f_{oc(m)}$$ (5-19)

where f_m is the fraction of the organic carbon (f_{oc}) attributed to sorbent m.

Multiple nonlinear isotherm models. Combinations of nonlinear isotherms are also possible. The cumulative sorbate concentration described with a multiple Langmuir isotherm model for N sorbents would be:

$$S = \sum_{n=1}^{N} \frac{K_{L\,(n)} \, S_{\max\,(n)} \, C}{1 + K_{L\,(n)} \, C}$$ (5-20)

This model has 2N fitted parameters $(K_{L(n)}$ and $S_{max(n)})$ and would approach a cumulative S_{max} at high C. Multiple Langmuir isotherms can combine to mimic a Freundlich isotherm (Weber, McGinley, and Katz 1992).

Multiple Freundlich models such as Kinniburgh (1986):

$$S = \sum_{n=1}^{N} \left(K_{F(n)} \, C \right)^{b_{F(n)}}$$ (5-21)

and Sheindorf, Rebhun, and Sheintuch (1981) are also useful in modeling heterogeneous sorbent systems. Again, the sum of Freundlich models has 2N adjustable parameters. The cumulative isotherm is not asymptotic but could appear nearly linear if the weighted divergence of b_F from 1.0 is fortuitously zero (e.g., equal concentrations of sorbents with $b_{F(1)} = 0.8$ and $b_{F(2)} = 1.2$).

These multiple sorbent models assume that each sorbent-sorbate equilibrium is independent or that each sorbent "sees" the same solute concentration. If one sorbent is more effective at scavenging the solute—perhaps due to faster adsorption kinetics—then a competitive sorbent model must be developed.

Distributed reactivity model. Weber, McGinley, and Katz (1992) propose a distributed reactivity model (DRM) that describes the composite, sorptive behavior of a soil system as the combined effects of simultaneous linear and Freundlich isotherms:

$$S = \sum_{n=1}^{N} x_n \, K_{d(n)} \, C + \sum_{m=1}^{M} y_m \, K_{F(m)} \, C^{b_{F(m)}} \qquad (5\text{-}22)$$

where x_n and y_m are the mass fractions of the nth linear and m^{th} nonlinear sorbing components. Although any number of components could be included in this model the authors suggest that practical difficulty in resolving multiple nonlinear components typically limits M to only 1 or 2. Weber, McGinley, and Katz (1992) preferred a Freundlich model to describe nonlinear reactions, noting that "Langmuir behavior is rarely observed even for the most homogeneous of soils" and that multiple Langmuirs could mimic a Freundlich isotherm. The sum of Freundlich expression in Equation 5-22 is slightly different than that described in Equation 5-21 (and Table 5.2) reads in which constituent sorbent mass fractions are implicit.

Weber, McGinley, and Katz (1992) demonstrated that small fractions of nonlinearly sorbing constituents can significantly affect the composite sorption behavior. Although the soils could be fitted to a single Freundlich expression, it is at the loss of flexibility in characterizing the sorption process. Sorption behavior of three chlorinated solvents on six sandy soil samples with f_{oc}s from 0.0003 to 0.025 was examined using the DRM. Sorbent heterogeneity was indicated by the observed range of sorption capacities and nonlinearities. The type of organic sorbent, which they resolve into "soft" or "hard" (recalcitrant) classes based on resistance to oxidation, exerts a significant influence on both sorption capacity and heterogeneity. The hard carbon material isotherms were more nonlinear and represent only a few percent of the total soil sample, whereas the soft carbon isotherms were more linear. The subject soils were developed on glacial deposits and contained shale fragments, which were the soil constituent to which sorption was best correlated. The possibility that the shale fragments act as microaggregates imposing a physical nonequilibrium phenomena (Section 5.5) was not considered, but the authors hint that they plan to address that possibility.

Competitive sorption models

Competition for sorption sites between the multitude of solutes in natural groundwaters should be expected. The assumption of ideal solute behavior is very appealing in light of the simplicity it affords the process modeler but is often made without adequate verification. There are few attractive alternatives to this assumption, since a practical, generally applicable, competitive sorption model is not available. However, as solute concentrations and/or heterogeneity increase, so does the probability of solute-solute or sorbate-sorbate interactions and perhaps competition for reaction sites. This caveat is particularly apropos in the case of polar and ionic solutes, which tend to be involved in more complexation reactions than nonpolar solutes. Competitive sorption mechanisms have been suggested to account for certain XAC interactions (Leggett 1985, Loehr 1989, Brannon et al. 1992).

Kinniburgh (1986) suggests that most of the equilibrium isotherms listed in Table 5.2 can be adapted to accommodate competitive sorption by replacing the aqueous concentration terms with a concentration (molar) or activity ratio, though he does not discuss the form of this ratio. A selectivity coefficient (K_S) approach modified for uncharged species may be appropriate:

$$K_s = \frac{X_{SN} [M]}{X_{SM} [N]}$$

(5-23)

analogous to the equation used to characterize ion exchange equilibria (Equation 5-4). Perhaps selectivity for solutes by a given sorption mechanism (e.g., H-bonding between surface hydroxyls and aromatic π electrons) is dependent on some quantifiable, structural, or electrochemical parameter, which would replace the exponents m and n in Equation 5-4.

A more general approach would be to incorporate the kinetics of each sorbent-sorbate reaction mechanism expected to be dominant for a given system into a multisorbent and/or multicomponent model. This model would be a major undertaking, which is one reason why no such model exists for organics, but benefits of developing a truly predictive model would be tremendous.

Competitive Langmuir model (implicit-adsorbate). In most sorption models, any displaced ions or ligands are neglected in deference to the adsorbing contaminant of interest. Curl and Keoleian (1984) refer to the displaced species as the implicit adsorbate, since its identity and concentration are not determined.

Curl and Keoleian (1984) and Keoleian and Curl (1989) present a competitive Langmuir isotherm model to illustrate the competitive sorption process. Adsorbate concentrations (S_j) for solute j in a mixture of k components may be described by:

$$S_j = \frac{K_{L(j)} \, S_{max(j)} \, C_j}{1 + \sum_{j=1}^{k} K_{L(j)} C_j}$$

(5-24)

Specifically, the explicit- (S_{ex}) and implicit-adsorbate (S_{im}) concentrations are:

$$S_{ex} = \frac{K_{L(ex)} \, S_{max(ex)} \, C_{ex}}{1 + K_{L(ex)} \, C_{ex} + K_{L(im)} \, C_{im}} \qquad (a)$$

(5-25)

$$S_{im} = \frac{K_{L(im)} \, S_{max(im)} \, C_{im}}{1 + K_{L(ex)} \, C_{ex} + K_{L(im)} \, C_{im}} \qquad (b)$$

where the *ex* and *im* super- and subscripts refer to explicit and implicit adsorbate. The implicit sorbate model uses a two-site isotherm with Langmuir and

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linear components. The competitive sorption model is used primarily to show that this mechanism can account for adsorbent-concentration effects and adsorption-desorption hysteresis, not that this is the best or only modeling approach. They suggest that the implicit sorbate should be identified and quantitated to obtain unique model parameters and to evaluate competitive sorption models.

Competitive Freundlich model. Sheindorf, Rebhun, Sheintuch (1981) derive a multicomponent sorption model for J constituents, each of which individually conforms to a Freundlich isotherm model. The adsorbate concentrations (S_i) for constituent i in a mixture is:

$$S_i = K_{F(i)} \, C_i \left[\sum_{j=1}^{J} a_{ij} \, C_j \right]^{n_i - 1} \tag{5-26}$$

where a_{ij} are the competition coefficients for components i and j $(a_{ij} = 1)$. The multicomponent Freundlich parameters, $K_{F(i)}$ and n_i, are identical to the single component isotherm values, which must be determined. For example, sorbate concentration for component 1 in a ternary mixture is:

$$S_1 = K_{F(1)} \, C_1 \left(C_1 + a_{12} \, C_2 + a_{13} \, C_3 \right)^{b_{F(1)} - 1} \tag{5-27}$$

Competition coefficients are determined for each binary interaction by fitting linearized forms of Equation 5-27 for bivariant concentrations:

$$\frac{C_1}{C_2} = \frac{1}{C_2} \, \beta_1 - a_{12}$$
$$\frac{C_2}{C_1} = \frac{1}{C_1} \, \beta_2 - a_{21} \tag{5-28}$$

or varying one concentration:

$$C_1 = \beta_1 - a_{12} \, C_2 \quad and \quad C_2 = \beta_2 - a_{21} \, C_1 \tag{5-29}$$

where:

$$\beta_i = \left[\frac{K_i \, C_i}{S_i} \right]^{\frac{1}{1-n_i}} \tag{5-30}$$

Although a_{12} equals $1/a_{21}$, determination of each provides a check on parameter validity. The model performed very well in describing multicomponent sorption of polar and ionic organic solutes (p-nitro- and p-bromophenol, or acetone and propionitrile) on activated carbon.

Equilibrium isotherms for explosives

A considerable body of research is available describing the equilibrium sorption of explosives (primarily TNT and RDX) on soils and manufactured sorbents. Much less sorption data are available for other explosives (e.g., HMX), and there is a dearth of information on the sorptive behavior of most other XACs, such as amino or azo transformation products. Insights as to the sorption mechanisms affecting XACs can also be gained by examining the sorptive behavior of compounds with similar structural elements, e.g., other nitro- or amino- compounds (Graveel, Sommers, and Nelson 1985, Zachara, Ainsworth, and Smith 1990, Zachara et al. 1986, Haderlein and Schwarzenbach 1993, Means and Wijayaratne 1989).

Most investigations of TNT sorption report less than 100 percent recovery of the adsorbed mass. In studies including both sterile ($HgCl_2$-suppressed microbial activity) and nonsterile adsorption-desorption experiments, much of the "lost" solute is attributable to microbially mediated transformations (e.g., Spanggord et al. 1980b, Pennington and Patrick 1990). Irreversible sorption was commonly suggested to account for much of the remaining lost solute, though direct verification is lacking due to the difficulty in analyzing bound materials. The transformation and binding of explosives is discussed further in Chapters 7 (microbial) and 8 (abiotic). Brief summaries of several of the major investigations of XAC sorption are presented below.

Spanggord et al. Spanggord and associates (e.g., Spanggord et al. 1980a,b, and 1981) conducted a series of investigations for the U.S. Army Medical Research and Development Command (Ft. Detrick, Maryland) to compile known or estimated chemical and environmental properties for munition wastes. For most of the XACs, sorption was considered to affect the environmental fate and transport much less than other surface processes, particularly photooxidation and biotransformation. Since sorption was considered moderate (most measured K_ds < 100), a linear partitioning model dependent on soil organic carbon content was generally advocated. This work was conducted with surface water transport in mind. Spanggord et al. (1980b) recognized that sorption would become more relevant if other processes became impaired.

Pennington and Patrick on TNT. Pennington (1988) and Pennington and Patrick (1990) evaluated TNT sorption onto soils from 13 Army Ammunition Plant (AAP) facilities, including the CAAP and LAAP discussed in Chapter 2. The sorption behavior was best described by Langmuir isotherms over the concentration range of 1.0 to 16 $\mu g \, mL^{-1}$. Correlation coefficients (r^2) were greater than 0.97 (10 of 14 above 0.99), S_{max} values ranged between 65 and

107 $\mu g \cdot g^{-1}$, and the K_L's were between 0.047 and 0.229. Freundlich isotherms fit the data slightly less well, with r^2's between 0.88 and 0.97, b_F values between 0.632 and 0.733, and the K_F's between 5.2 and 16.3. Linear isotherms fit the data relatively poorly, with r^2's between 0.88 and 0.94; the K_d's ranged between 2.28 and 6.83.

The subject soils contained fairly high organic carbon fractions (f_{oc}) between 0.367 and 3.592 percent. The higher f_{oc}'s were associated with stronger TNT partitioning, as would be expected for hydrophobic organic solutes. However, Pennington and Patrick (1990) observed positive correlations between TNT sorption, as represented by a single K_d value (average approximately 4.0), and extractable iron (Fe) content, cation exchange capacity (CEC), clay content, and soil organic carbon content, listed in decreasing order of correlation coefficients (r^2 = 0.79, 0.76, 0.49, and 0.16, respectively). Sorption mechanisms other than hydrophobic partitioning are operative in TNT sorption.

It is difficult to interpret such correlations since the soil parameters are certainly not independent, i.e., they may arise from the same soil feature (for example, iron, clay, and soil organics all contribute to the CEC). Although correlation with total f_{oc} was weak, the emerging model for XACs sorption suggests that a bulk mass fraction f_{oc} may be less relevant than some assessment of the functional group populations characterizing the soil organic. If, for example, TNT nitro groups or π bonds show an affinity for particular humic acid functional groups (e.g., carboxyls), then correlation against the specific group concentration would be more appropriate. Soil humic compositions may vary dramatically, even at a single field site (e.g., Sposito 1986).

Reducing conditions (Eh = -150 mv) consistently enhanced adsorption relative to oxidizing conditions (Eh = +450 mv). An important implication for remediation modeling is that sorption could be enhanced if the aerobic biotransformations associated with in situ biotreatment drive the system anaerobic. Partial, microbial reduction of TNT nitro groups (Ar–NO_2) to amino groups (Ar–NH_2) was indicated by the appearance of 4–amino-2,6–dinitrotoluene (4A–2,6–DNT) and 2–amino-4,6–dinitrotoluene (2A–4,6–DNT). The production of amino compounds in sterile systems ($HgCl_2$ treated) suggests that an abiotic mechanism may also be operative (see Chapter 8). No significant pH effects on sorption were detected, based on batch sorption and sequential desorption experiments at pHs 5.0, 6.5, and 8.0.

Sorption was reported to be completely reversible for the 2-hr exposure times utilized for sediment loading. Sorption of TNT was not considered sufficiently strong to significantly retard its transport to lower soil horizons.

Leggett on TNT, DNT, RDX, and HMX. Leggett (1985) described linear adsorption isotherms for RDX and HMX over concentration ranges of

0 to 15 mg·L^{-1} and 0 to 1.9 mg·L^{-1}, respectively, on commercial bentonites.[1] Isotherms for TNT (0 to 10 mg·L^{-1}) and DNT (0 to 2.5 mg·L^{-1}) were nonlinear. Based on a Scatchard analysis and thermodynamic arguments, Leggett suggests that the TNT (and DNT) isotherm may be resolved into two components, fitting a Langmuir model at low sorbate levels, and a linear model at high sorbate concentrations. This duality is interpreted as the effect of two, simultaneous, sorption mechanisms:

a. Specific, moderately high energy (42 kJ·mol^{-1}) bonding, attributed to hydrogen bonding with surface hydroxyl groups and/or interactions between the negatively charged clay surfaces and the aromatic π bonds.

b. Nonspecific or hydrophobic type bonding which contributes to TNT and DNT adsorption and dominates RDX and HMX (nonaromatic) sorption.

The specific mechanism(s) appear to be more important for the nitroaromatics (TNT and DNT) than for the saturated nitrogen heterocyclics (RMX, HMX). Leggett attributes the more energetic bonding of the nitroaromatics to the presence of multiple, electronegative, nitro groups which draw electrons out of the π bonds (internal charge transfer), thereby enhancing the hydrogen bonding or donor-acceptor reactions between the nitroaromatic and the cation exchange site of the bentonite. This mechanism would not be active for the saturated ring heterocyclics (RDX, HMX). Leggett (1991) expanded this discussion of possible electron donor-acceptor reactions between nitroaromatics and soil components.

Leggett (1985) observed some competition between TNT and DNT for sorption sites, with the bentonites showing a preference for TNT. This observation would be consistent with the π bond - clay interaction model, since TNT has one more nitro group than DNT. No indication of sorption competition between RDX and HMX was detected, presumably due to their much lower concentrations.

Ainsworth et al. on TNT and RDX. In 1993 Ainsworth and associates developed an empirical descriptor for TNT and RDX sorption as a function of several soil parameters. They evaluated batch and column sorption behavior for a number of soils characterized with respect to percent soil organic carbon (*%OC*), percent clay-size particle content (*%clay*), extractable iron (*DCB-Fe*; dithionate-citrate-bicarbonate as extractant), *pH*, and *CEC*. RDX showed linear isotherms and an expression to predict a K_d was proposed:

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[1] Bentonite is a common, drilling mud used to enhance borehole stability and removal of cuttings; dominant constituents are expandable clay minerals, e.g., montmorillonite. Many commercial bentonites contain proprietary additives (e.g., organic polymers), which could complicate the interpretation of isotherms.

$$K_d = -0.38 + 0.149 \ (\%OC) + 0.008 \ (\%clay) \qquad (5\text{-}31)$$
$$-0.0006 \ (DCB\text{-}Fe) + 0.074 \ (pH) + 0.033 \ (CEC)$$

Predicted K_d's were within a factor of 2 to 2.25 of measured values. Column breakthrough experiments with RDX showed approximately symmetrical sorption (leading) and desorption (tailing) limbs. The RDX sorption is affected by OC but also by other mechanisms. Sorption at various temperatures indicated RDX adsorption to be slightly exothermic ($\Delta H_r = -10$ to -20 kJ·mol^{-1}, consistent with hydrogen bonding or van der Waals forces).

TNT sorption was best fit with a Freundlich isotherm expression. The proposed empirical expressions for the Freundlich parameters are (Ainsworth et al. 1993):

$$K_f = -7.69 + 1.6 \ (pH) + 0.035 \ (CEC) \qquad (5\text{-}32)$$
$$1/n = +0.56 + 0.15 \ (\%OC)$$

The predicted K_f values were within a factor of 3.5 (most within a factor of 2) of the observed value. Predicted values for $1/n$ were more variable. The TNT loss observed in both batch and column experiments was attributed to abiotic reduction; amino and diamino compounds were generated (see Chapter 8). Column breakthrough curves showed asymmetric sorption and desorption limbs and were more asymmetrical at lower flow velocities. The TNT adsorption was slightly more exothermic than RDX ($\Delta H_r = -25$ kJ·mol^{-1}, also consistent with hydrogen bonding or van der Waals forces). These sorption experiments with TNT and RDX indicate differences in sorption mechanisms but do not provide insight as to the specific reaction mechanisms involved such as TNT transformation.

Loehr on TNT, DNT, RDX. Loehr (1989) fits Freundlich isotherms (see Table 5.3) to batch adsorption data for 2,4-DNT (15-160 mg·L^{-1}) and 2,6-DNT (14-600 mg·L^{-1}) on a sandy silt loam ("Texas soil": $f_{oc} = 0.0325$, pH $= 7.8$) and a sandy loam ("Mississippi soil:" $f_{oc} = 0.0094$; pH$=4.8$). The RDX and HMX did not fit the Freundlich model well ($r^2 < 0.44$). The HMX solubility was too low for reliable sorption experiment analyses with the analytical method utilized (HPLC; detection limit 1 mg/L).

Table 5.3
Summary of Batch Isotherm Data for DNT's[1]

Soil Type	Compound	K_F	b_F	r^2	pH
Texas Soil	2,4-DNT	9.2×10^{-3}	0.59	0.88	7.6
	2,6-DNT	5.0×10^{-3}	0.61	0.90	8.1
Mississippi Soil	2,4-DNT	6.3×10^{-3}	1.08	0.99	5.2
	2,6-DNT	14.0×10^{-3}	0.68	0.95	5.6

[1] From Loehr (1989).

Sorption behavior for TNT was not consistent with existing isotherms; sorbate concentrations showed a maximum at S = 0.045 $mg_{TNT} \cdot g^{-1}_{soil(dry)}$ and C $\approx$ 15 $mg \cdot L^{-1}$; sorbate concentration decreased at higher solute concentration. Loehr (1989) did not speculate as to the cause of the nonmonotonic sorption isotherms. Assuming the phenomenon is not due to experimental design flaws, perhaps the anomalous behavior is caused by:

a. *Competitive sorption with an implicit adsorbate.* The nitroaromatics were able to displace the implicit adsorbates only at higher concentrations.

b. *Physical nonequilibrium effects.* If the soil particulates were microporous, and the rate of diffusive mass transfer into these particles is concentration dependent, then more would be "lost" from solution at higher concentrations. The cyclic compounds were not affected because of steric exclusion from the micropores.

c. *Aqueous cluster formation.* Aqueous complexes involving TNT formed at higher concentrations (analogous to a critical micelle concentration).

Brannon et al. on TNT and RDX leaching. Brannon et al. (1992) report anomalous adsorption behavior for TNT and RDX on various materials (silty soil, sand, activated carbon, and lake sediment "muck"). Radio-labeled TNT adsorption kinetics indicate rapid and complete initial uptake (by day 1), but then a reappearance of ^{14}C in solution by day 30, followed by a gradual and consistent trend in ^{14}C readsorption. Brannon et al. (1992) speculate that the peculiar adsorption behavior may be related to:

a. *Competitive sorption.* The initial rapidly adsorbed TNT is subsequently displaced by an implicit sorbent.

b. *Abiotic transformation.* The TNT is transformed to a more soluble form (e.g., amino compound), which is then slowly sorbed to the solid.

c. *Initial association with a labile component.* Rapid TNT partitioning into another phase would account for early disappearance; breakdown of the implicit phase releases TNT to solution from which it slowly readsorbs.

Several additional mechanisms are also possible. Perhaps the phenomenon is an artifact of the TNT spiking technique (introduced to vessel walls prior to adding soil); it may be that 1 day was insufficient to attain equilibrium partitioning of TNT from the reaction vessel walls. Alternatively, if the sterilization by gamma radiation lyses some of the bacterial cells, enzymes released could complex with TNT, releasing TNT upon subsequent degradation. This process would be consistent with the "labile component" hypothesis. RDX sorption was also anomalous; aqueous concentrations are initially high,

dropped by day 30, up again by day 90, then down slowly by days 180 and 270.

The possibility of multiple, speculative interpretations suggests that adsorption experiment procedures should be redesigned to eliminate or reduce the ambiguity. For example, since solutes are quantified by liquid scintillation counting of the ^{14}C ring-labeled solutes, the specific structure of the possible alteration compounds is unknown. Thus, the nature of transformation reactions cannot be evaluated. Liquid scintillation should be combined with a chromatography technique (HPLC) in order to identify transformation products (biotic or abiotic).

5.3 Nonequilibrium Sorption Processes

The preponderance of evidence from laboratory and field observations indicates that local equilibrium is not always attained. Therefore, any invocation of the local equilibrium assumption should be justified, or at least the potential for error understood. Nonequilibrium is attributed to one or more processes of a chemical or physical nature. Chemical nonequilibrium sorption (Section 5.4) is due to sorption reaction rates that may not be treated as instantaneous relative to advective transport rates. Physical nonequilibrium sorption (Section 5.5) results from the permeability and/or mineralogy contrasts so pervasive in subsurface media at all scales (micropore to lithofacies). The current consensus is that solute diffusion phenomena (physical nonequilibrium process) are the rate-limiting processes affecting the sorption of organic contaminants, but there is no consensus as to the dominant mechanism or appropriate modeling approach to characterize these processes (Miller and Pedit 1992, Harmon, Ball, and Roberts 1989, Brusseau and Rao 1989a).

Bench-scale evidence. At the bench (laboratory) scale, nonequilibrium phenomena are evident from the growing recognition of the following:

   a. Solute sorption, even in batch reactors, is not necessarily instantaneous and may require very long contact time to approach true equilibrium.

   b. Breakthrough curve (BTC) tailing is not completely attributable to nonlinear sorption isotherms.

Innumerable reports observe that organic solute adsorption is characterized by rapid initial uptake, followed by a period of slower adsorption (e.g., Karickhoff, Brown, and Scott 1979). Several researchers have observed further that truly equilibrated partitioning for many, natural solute-sorbent systems may require on the order of 100's of days (Ball and Roberts 1991a,b; Brusseau and Rao 1989a), rather than the 1-2 days commonly considered as "close enough" to equilibrium (Spanggord et al. 1980a,b; Pennington and Patrick 1990).

The mass transfer rate of solute from the aqueous phase to the solid phase in adsorption batch tests tends to decrease quite rapidly with exposure time. Typically, on the order of 20 to 50 percent of the total mass adsorbed is taken up in the first minutes to hours. Total equilibrium may not be achieved for days to months. This commonly observed behavior has been interpreted as representing a two-stage (series) or two-component (parallel) kinetic process. The rapid initial rates are attributed to the filling of previously unoccupied sites (or occupied weakly) and/or surfaces that are readily accessible, e.g., at grain surfaces. The slow uptake is attributed to either chemical or physical causes, both of which are reviewed below. (Karickhoff 1980, Brusseau and Rao 1989a, Ball and Roberts 1991a,b).

Solute transport through packed columns of aquifer or soil material, as revealed by effluent concentration history (breakthrough curves or BTCs), often shows the tracer arriving faster than would be expected based on the advection-dispersion equation. Subsequent miscible displacement of the solute-bearing water by clean water often shows tracer effluence well behind that which is attributable to simple dispersion. Nonlinear sorption isotherms may account for some tailing (e.g., Freundlich $K_F < 1$; or Langmuir) or early breakthrough ($K_F > 1$). Isotherm nonlinearity does not account for all of the BTC asymmetry. The BTC asymmetry may be due to hydrodynamic dispersion alone, as when the Peclet number (Pe $\equiv$ vL/D) is less than 10 (Brusseau and Rao 1989a).

Field-scale evidence. Field evidence of nonequilibria includes the apparent rate-limited recovery of contaminants under pump-and-treat remediation schemes. Initial plume recovery may show high levels of contaminant, which decrease as the affected zone is swept with clean water. Yet, if withdrawal is ceased for a period of days to weeks and then restarted, very often the solute levels have increased dramatically. This rather frustrating, nonequilibrium phenomenon generally is attributed to a diffusive rate-limiting process and is a major impetus for the current active research to quantitate and/or overcome the effects of media heterogeneity on remediation.

The net effect of nonequilibrium sorption is to accentuate dispersion. The relative importance of hydrodynamic dispersion and nonequilibrium dispersion must be elucidated by inclusion of a conservative solute in displacement experiments. Chemical nonequilibrium would not affect net retardation as defined based on the first moment of the BTC.

Discerning the rate-limiting processes affecting the XAC fate and transport is critical to the remediation of contaminated sites and predictive remediation modeling. Recognition of the potential sources of nonequilibrium behavior is essential. Understanding the controls on the nonequilibrium behavior is the only way to hypothesize as to possible rate-limiting, sorption mechanisms in a given case. Once these mechanisms are established, technologies to control or influence these subsurface processes can be engineered and implemented.

Many conceptual, mathematical, and numerical models, much too numerous to review completely, have been proposed over the last three decades to describe rate-limited (kinetic) sorption behavior. These models can be classified broadly into either chemical or physical process models, as well as hybrid models. Chemical process models describe sorption as controlled by one or more kinetic adsorption/desorption processes. These models differ based on the type of rate expression invoked and the number of active sorbents or sorption site classes. Physical process models attribute the nonequilibrium behavior to mass transfer between two or more regions within the porous medium continuum. The physical models differ primarily based on the number and geometry of regions and the formulation for the inter-region mass transfer descriptor. Hybrid models combining chemical and physical processes have also been formulated.

5.4 Chemical Nonequilibrium Models

Chemical nonequilibrium sorption models envisage partitioning as being affected by two or more sorption reactions (e.g., adsorption and desorption), at least one of which is rate-limited. The rate of any particular sorption reaction depends on the nature of the solute (charge, polarity, hydration, or complexation condition, etc.), the sorbent (surface charge, presence of competing adsorbate, etc.), and the environmental conditions (e.g., temperature, pressure, pH). Steric hindrances may impede certain sorption processes with large molecules. Early (before circa 1975) and simple kinetic models which considered only single-site reactions could not represent many natural sorption phenomena well. Multisite models are better equipped to simulate the natural, heterogeneous sorbent-sorbate system.

Sorption kinetics

Prior to introducing chemical process descriptors, a brief overview of kinetics modeling is in order. The kinetic rate laws outlined below are also drawn upon in the discussion of other rate-limited processes, such as biotransformation (Chapter 7), abiotic reactions (Chapter 8), and XAC dissolution (Chapter 4).

Numerous rate laws have been developed or adapted to describe the kinetics of biogeochemical processes. Reaction rates which are independent of concentration are zero order (e.g., reactant present in great excess relative to reaction rate; a special case in biotransformation). First-order reaction rates depend on the concentration of one of the reactants (e.g., radioactive decay, common model for adsorption or biotransformation). Second-order and higher (n^{th}-order) reaction rates depend on the concentration of 2 (to n) reactants or products (e.g., ion exchange). The list of rate law expressions in Table 5.4 is presented here only to indicate the diversity of rate law expressions. Only a few of these rate expressions are actually utilized commonly in contaminant transport modeling. Skopp (1986) notes that when combining

chemical rate expressions with transport equations, solutions tend to become less unique. Therefore he wisely suggests consideration of multiple, alternative, rate expressions, or a combination of several types of kinetics when developing descriptors for rate-limited processes in order to avoid model myopia.

Table 5.4
Empirical, Kinetic Rate Laws[1] for the Stoichiometric Reaction

$$a\,A + b\,B \overset{k_f}{\rightleftharpoons} c\,C + d\,D$$

Forward Reaction Rate Expression[2]	Description	Common Applications
$-\,k_o$	Zero-order reaction	Special case for biodegradation (excess reactant)
$-\,k_1\,A$	First-order reaction	Radioactive decay, adsorption, biotransformation
$-\,k\,A^j$	jth-order reaction	Freundlich isotherm
$-\,k\,A\,B$	Second-order overall; first-order with respect to A or B	Ion exchange; SOTS
$-\,k\,A^j\,B^i$	$(j+i)$-order reaction overall	
$-\,k\,A^f$	Fractal order f reaction; f $\neq$ integer	
$-\,k\,A^f\,B^g$	Fractal order f, g $\neq$ integer	
$-\,k_i\,A\,/\,(k_j + A)$	Michaelis-Menten kinetics	Substrate utilization by microbes (see Chap. 7)
$-\,k_i\,/\,(k_j + A)$	Two-term denominator	
$-\,k\,\exp\,[-k_e\,A]$	Elovich equation	Irreversible sorption
$-\,k\,A^f\,C^g$	Feedback approximation	

[1] Modified from Skopp (1986).
[2] Integer superscripts i and j may be negative.

Many of the equilibrium sorption models discussed in Section 5.3 (see Table 5.2) may also be expressed in a kinetic form (Table 5.5 below). Several of these kinetic models are discussed below.

Single-site kinetic models

One of the simplest models that begins to describe time-variable, sorption phenomena is the first-order, single-site model:

Table 5.5
Summary of Representative Kinetic Sorption Models[1]

Isotherm	Equation[2]	Number of Kinetic Parameters	Reference[3]
Linear or First Order	$$\frac{\partial S}{\partial t} = \left[\frac{n_e}{\rho}\right] k_1 C - k_2 S$$	2	S,RJ
n[th]-Order (in C)	$$\frac{\partial S}{\partial t} = \left[\frac{n_e}{\rho}\right] k_1 C^N - k_2 S$$	2	S
Power $(N+M)$[th]-order	$$\frac{\partial S}{\partial t} = \left[\frac{n_e}{\rho}\right] k\, C^N S^M$$	3	S
Langmuir (L)	$$\frac{\partial S}{\partial t} = k_r \left[\frac{K_L S_{max} C}{1 + K_L C} - S\right]$$	2	RJ
	$$\frac{\partial S}{\partial t} = \left[\frac{n_e}{\rho}\right] k_1 C \left(S_{max} - S\right) - k_2 S_2$$	2	S
Freundlich (F)	$$\frac{\partial S}{\partial t} = k_r \left(K_F C^{b_F} - S\right)$$	2	RJ
Two Site Freudlich	$$\partial S/\partial t = \partial S_1/\partial t + \partial S_2/\partial t$$ where $$\partial S_1/\partial t = k_1 C^{k_2} \partial C/\partial t$$ $$\partial S_2/\partial t = k_r \left(k_1 C^{k_2} - S_2\right)$$	2	RJ
Irreversible (source/sink)	$$\frac{\partial S}{\partial t} = k_1 \frac{n_e}{\rho} \left(C - C_p\right)$$	1	S
Elovich	$$\frac{\partial S}{\partial t} = A \exp\left[-B\, S\right]$$	2	S
Mass Transfer	$$\frac{\partial S}{\partial t} = k \frac{n_e}{\rho} \left(C - C^*\right)$$	1	S

[1] Modified from Selim, Davidson, and Iskandar (1990) and Rao and Jessup (1982); see Table 5.2 .
[2] Key: S = sorbate concentration; C = solute concentration; C_p = equilibrium saturation concentration; C^* = solute concentration in region of S (associated C in mixed zones); k, k_r, k_1, k_2 = reaction rate coefficients (subscripts 1,2 for constituents); K_F, b_F = Freundlich coefficients; K_L = Langmuir coefficients; S_{max} = maximum sorbate concentration.
[3] References: RJ = Rao and Jessup (1982); S = Selim, Davidson, and Iskandar (1990).

$$\frac{\partial S_i}{\partial t} = k_1 \frac{n_T}{\rho_b} C_i - k_2 S_i$$

<div align="right">(5-33)</div>

for which k_1 and k_2 are the adsorption and desorption rate constants [T^{-1}], respectively (Brusseau and Rao 1989a). This one-box model (see Figure 5.2) shows that the rate of sorption is a first-order function of concentration (or fugacity) contrast between the sorbed and dissolved state. The rate constants may be defined from one rate constant (e.g., k_1) and the equilibrium partitioning coefficient (i.e., $k_2 = K_P / k_1$). The rate constants are independent of concentration, and the sorbent and solution "boxes" are treated as well-mixed. Unfortunately this simple model does not predict experimental data well (Wu and Gschwend 1986, 1988; Brusseau and Rao 1989a).
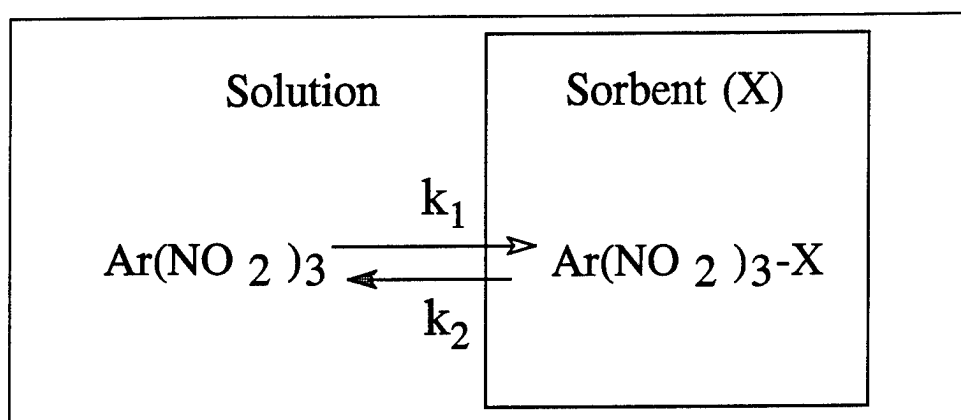
Figure 5.2. Schematic diagram of the single-site sorption kinetics model (Equation 5-33)

Two-site kinetic models

Several researchers have adopted a two-site modeling approach to capture the superficially dichotomous, sorption behavior often observed in batch adsorption experiments—the rapid, initial uptake, followed by a slow approach to equilibrium. One class of sites (or sorbent) reaches equilibrium instantaneously, or relatively quickly; a second class is characterized by slower sorption.

Selim, Davidson, and Mansell (1976) and Cameron and Klute (1977) were among the first to describe semikinetic models with two classes of sites—type-I represents the "fast sites" controlled by equilibrium partitioning, and type-II represents the "slow sites" for which a first-order (or other) kinetics model is invoked. The two sorbed components are described as:

$$\frac{\partial S_T}{\partial t} = \frac{\partial S_I}{\partial t} + \frac{\partial S_{II}}{\partial t} \qquad \qquad (5\text{-}34)$$

where

$$\frac{\partial S_I}{\partial t} = \frac{n_e}{\rho} k_1 C - k_2 S_I \qquad (a)$$

$$\frac{\partial S_{II}}{\partial t} = \frac{n_e}{\rho} k_3 C - k_4 S_{II} \qquad (b)$$

$$(5\text{-}35)$$

The schematic diagram of the two-site model (Figure 5.3) serves as a basis for discussion of several specific models.
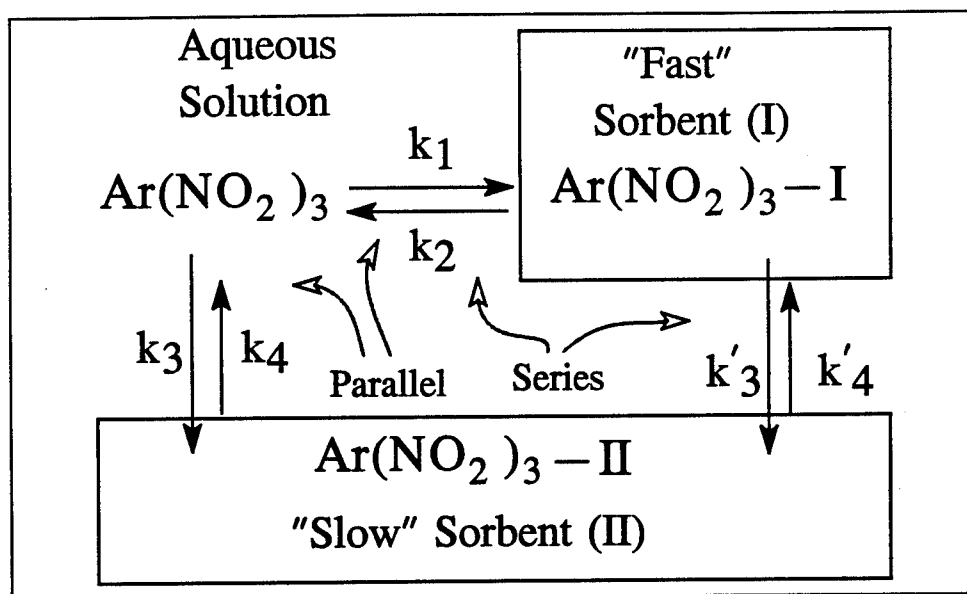
Figure 5.3. Schematic diagram of a two-site sorption model (Equation 5-35)

At equilibrium the derivative terms in Equations 5-35a and 5-35b are zero, and:

$$S_I = \frac{n_e k_1}{\rho k_2} C_i = K_I C \qquad (a)$$

$$S_{II} = \frac{n_e k_3}{\rho k_4} C_i = K_{II} C \qquad (b)$$

$$(5\text{-}36)$$

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where K_I and K_{II} are the equilibrium partitioning coefficients for sites I and II, respectively. Expressing the equilibrium isotherms with Freudlich models, Equation 5-34 becomes:

$$\frac{\partial S_T}{\partial t} = \left[\frac{n_e}{\rho} k_{FI} C^N - k_2 S_I \right] + \left[\frac{n_e}{\rho} k_{F3} C^M - k_4 S_{II} \right] \qquad (5\text{-}37)$$

where $F1$ and $F3$ are Freundlich coefficients, and the superscripts N and M denote the order of the sorption rate expressions for type I and II sites, respectively. Selim, Davidson, and Mansell (1976) note that these exponents are typically less than 1.0. If the type-I sites are taken to be rapidly equilibrating sites, then Equation 5-37 can be simplified somewhat to:

$$\frac{\partial S_T}{\partial t} = \left[\frac{n_e}{\rho} N K_I C^{N-1} \right] \frac{\partial C}{\partial t} + \left[\frac{n_e}{\rho} k_3 C^M - k_4 S_{II} \right] \qquad (5\text{-}38)$$

where K_I is the equilibrium distribution coefficient for type-I sites ($K_I = n_e k_1 / (\rho k_2)$). Site-I partitioning could then be incorporated into a retardation factor similar to Equation 5-15. Selim, Davidson, and Mansell (1976) describe a numerical model retaining the flexibility of all four rate constants. Cameron and Klute (1977) present an analytical solution assuming linear Freundlich isotherms.

Karickhoff and Morris (1985) and Karickhoff (1980) proposed a simple two-site (or two-mechanism) sorption model for polynuclear aromatics hydrocarbon systems. Sorption to the "fast" (S_I or labile) sites is modeled as instantaneous and linear (described by partitioning coefficient, K_d). Mass transfer to "slow" sites (S_{II} or nonlabile) is modeled with a pseudo-first order rate constant (k_s):

$$
\begin{array}{ccccl}
& X_I K_d & & k_s & \\
C & \rightleftharpoons & S_I & \rightleftharpoons & S_{II} \qquad (a)\ series \\
& or & & & \\
S_I & \rightleftharpoons & C & \rightleftharpoons & S_{II} \qquad (b)\ parallel
\end{array}
\qquad (5\text{-}39)
$$
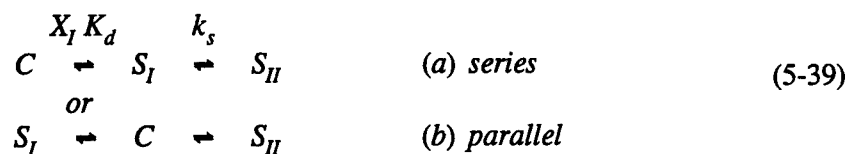
where X_I is the fraction of sorbed compound at fast sites. Since one K_d governed exchange between all compartments, one cannot distinguish between the proposed serial model (in Figure 5.3, $k_1 = k_2$, and $k = k'_3 = k'_4$) and an alternative, parallel conceptualization in which partitioning to each compartment is from the aqueous phase (in Figure 5.3, $k_1 = k_2$, and $k = k_3 = k_4$) (Pignatello 1989).

The two-site models capture the nonequilibrium breakthrough behavior much better than the single-site models. The multiple-site concept may be

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combined with other nonequilibrium models, e.g., physical nonequilibrium models (Section 5.5).

The first-order, two-site model of Selim, Davidson, and Mansell (1976) and the kinetic first-order, two-region sorption model (Section 5.5) of van Genuchten and Wierenga (1976) expressed in dimensionless forms are mathematically equivalent with respect to breakthrough curves (Nkedi-Kizza et al. 1984). Both models are empirical in their treatment of the slow loss of solute from solution (slow sites or immobile regions), and are not resolvable based on effluent (breakthrough) data. They are not equivalent with respect to in-column measurements as the dimensionless parameters are conceptually different.

There is no theoretical limit to the number of site classes that could be defined. In current practice, only two or three site types are modeled since the number of parameters that must be estimated increases with complexity and such complexity is seldom justified in terms of increased model accuracy, particularly in light of other uncertainties. Perhaps a sorbent-specific model could be developed based on sorptive behavior of XACs on a suite of individual standard sorbents (e.g., humics, iron oxyhydroxide, illitic clay minerals, etc.). Once kinetic models for individual sorbents are developed, bulk sorption behavior may be predicted from petrographic, chemical, and mineralogical analyses of the soil.

Second-order, two-site model

Selim and Amacher (1988) enhance the earlier two-site adsorption model (Selim, Davidson, and Mansell 1976) by imposing second-order sorption kinetic expressions. Their second-order, two-site (SOTS) model treats sorption kinetics as a function of both solute concentration and the proportion of available sites (ϕ_i, i = I or II), i.e., is first order in C and ϕ:

$$\frac{\partial S_I}{\partial t} = \frac{n_e}{\rho} k_1 \phi_1 C - k_2 S_I \qquad (a)$$

$$\frac{\partial S_{II}}{\partial t} = \frac{n_e}{\rho} k_3 \phi_{II} C - k_4 S_{II} \qquad (b)$$

$$(5\text{-}40)$$

where k_1 and k_2 are the adsorption and desorption rate constants, respectively, for type-I sites; likewise k_3 and k_4 are the analogous rate constants for type-II sites (see Figure 5.3). The site availability parameter (ϕ) is the difference between the fraction of total sites of the particular type and the number of occupied sites, e.g., for S_T total sites of which F are type I, $\phi_I = (F) (S_T - s_I)$; likewise, $\phi_{II} = [(1-F)S_T - s_{II}]$. If the site availability is not considered ($\phi_i = 0$, i = 1,2), the resulting first-order kinetic model does not capture the limit imposed by finite sorbent capacities. Setting k_1 and k_2 much greater ($10^{\geq 2}$) than k_3 and k_4 effectively makes the type-I sites equilibrium sites and type-II sites nonequilibrium sites, equivalent to simpler semikinetic two-site model.

Irreversible reactions (sink/source) are treated with a first-order kinetic expression (= k_sC).

Selim and Amacher (1988) incorporate a physical nonequilibrium, two-region, mass transfer capability into their SOTS model. The second-order mobile-immobile region (SOMIM) model does not significantly improve the predictions of metal transport investigated. This fact is attributed to a lack of physical nonequilibrium being a significant phenomenon in the media studied. Neither the SOTS or the SOMIM models consider competitive sorption or ion exchange.

Selim, Davidson, and Iskandar (1990) developed the highly flexible, multi-reaction transport model (MRTM) which simulates multiple, simultaneous, sorbate-sorbent interactions, including irreversible sorption sites (S_{irr}) and reversible sorption sites characterized by equilibrium kinetics (S_e), fast kinetics (S_1), and slow kinetics (S_2), through which other reversible sorption sites (S_3) may be accessed (Figure 5.4). This model includes most of the kinetic reactions discussed so far, exclusive of competitive sorption. The only rate expression which has not been described previously is that for $C \rightleftharpoons S_2$ when S_3 is present:

$$\frac{\partial S_2}{\partial t} = \frac{n_e}{\rho} k_3 C^M - k_4 S_2 - k_5 S_2 + k_6 S_3 \qquad (5\text{-}41)$$
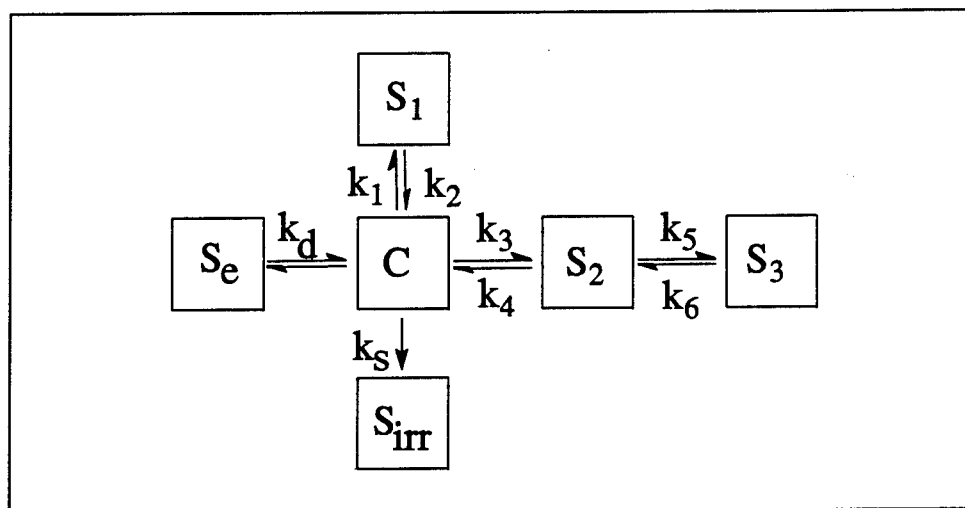
Figure 5.4. Schematic of sorbents (S) and rate coefficients (k) for the multi-reaction retention model (Selim, Davidson, and Iskandar 1990)

5.5 Physical Nonequilibrium Models

Natural porous media are intrinsically heterogeneous. These heterogeneities include both hydrogeologic heterogeneities (e.g., permeability contrasts) and biogeochemical heterogeneities (e.g., sorbent mineralogy). Physical nonequilibrium sorption models describe the nonequilibrium in terms of diffusion-limited mass transfer between one or more hydrodynamic regions. Delineation of these regions depends on the scale of the transport process being described. Of greatest concern here are zones of low permeability within or adjacent to zones of higher permeability (aquifers; "mobile water" regions). Contaminants diffuse into low permeability zones ("immobile water" regions) by the very slow process of molecular diffusion; complete diffusion back out during remediation may take even longer. Several examples of commonly encountered low permeability zones in sedimentary terranes include the following:

a. Fine-grained lithofacies, e.g., mudstone or shale stringers or strata within fluvial sands.

b. Stable soil aggregates or lithic fragments.

c. Hydrodynamic boundary layer or film at pore walls.

d. Dead-end micropores and microfractures in grains.

e. Intrasorbent porosity, e.g., soil organics, oxyhydroxides, expandable clays, zeolites.

These examples are listed in approximate decreasing order of physical scale. Mass transfer within or between any of these regions may be rate-limiting to the overall sorption process (Bales and Szecsody 1990, Coats and Smith 1964, Wood, Kraemer, and Hearn 1990, Brusseau and Rao 1989a,c, 1991). Schematic diagrams of the mobility regions and processes are presented in Figures 5.5 through 5.7. Descriptors are also available for cases in which a low permeability medium contains finite zones of high permeability, e.g., fractured porous media or soil macropores.

In principle, any number of regions could be defined for multiple interacting continua models, e.g., MINC concept of Narasimhan and Pruess (1988). Mobile water regions could also be subdivided into higher and lower permeability zones; immobile regions could be defined as some subset of those listed above. A three-resistance model could define mass transfer between regions of advective transport, intra-aggregate mesopores, and intraparticle micropores.

Natural sorption processes at the grain scale ($\leq$ 2 mm) involves mass transfer from a mobile water region to a sorbent surface through an immobile water region. The immobile water may be subdivided into a hydrodynamic surface film, intrasorbent pore water, and water adsorbed at the solid surfaces;
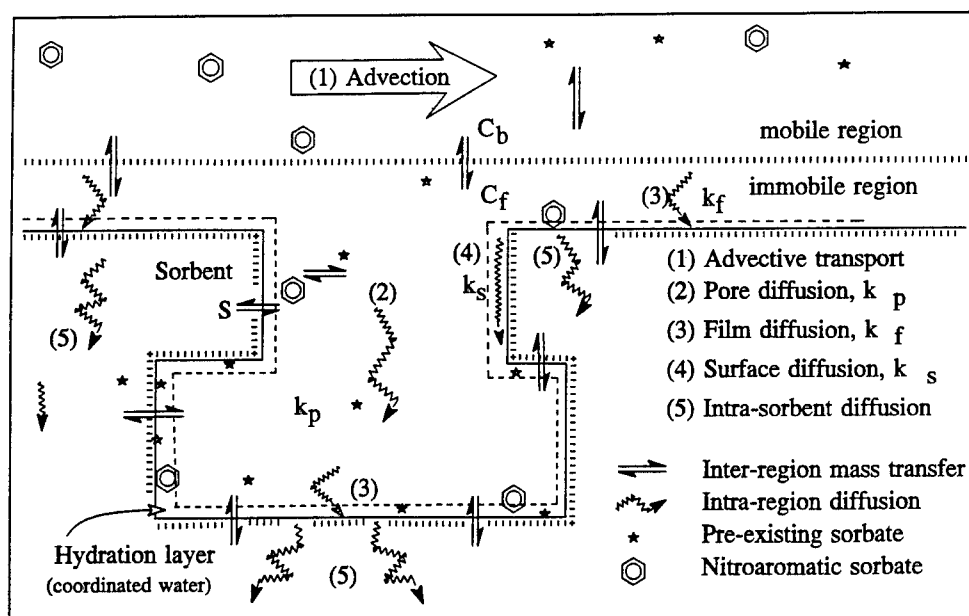
Figure 5.5. Schematic diagram of micropore structure and processes. Micropores are also present in the solids in Figure 5.6
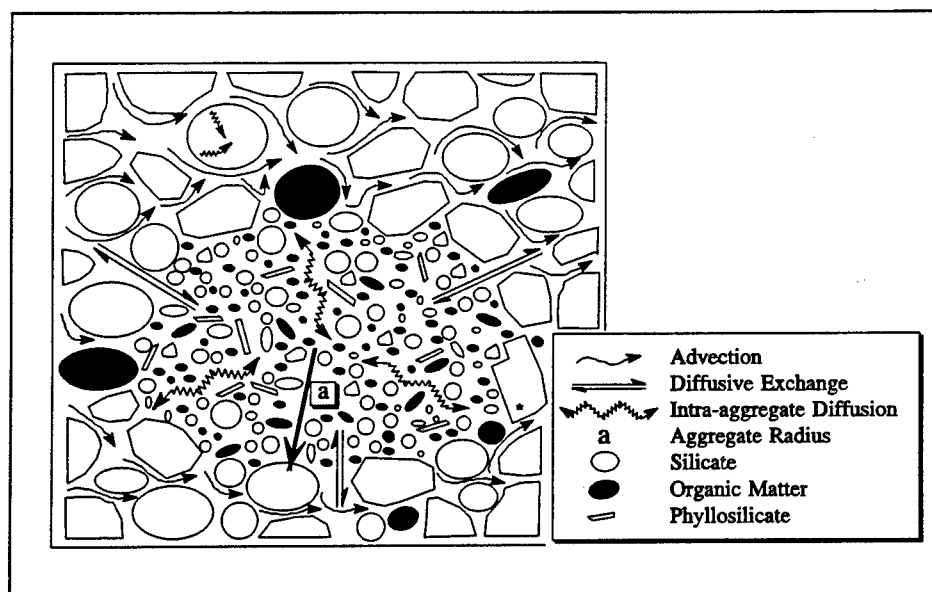
Figure 5.6. Schematic diagram of diffusive exchange through meso-pores of a fine-grained aggregate or lithic fragment

these are, respectively, the film, pore, and surface waters in Figure 5.5. The hydrodynamic film forms between the grain exterior and the adjacent mobile water; sorbate molecules traverse this region by film diffusion (process 3 in Figure 5.5). Subsequently, sorbate molecules can diffuse through unbound water within grain micropores (intrasorbent pore diffusion; process 2 in

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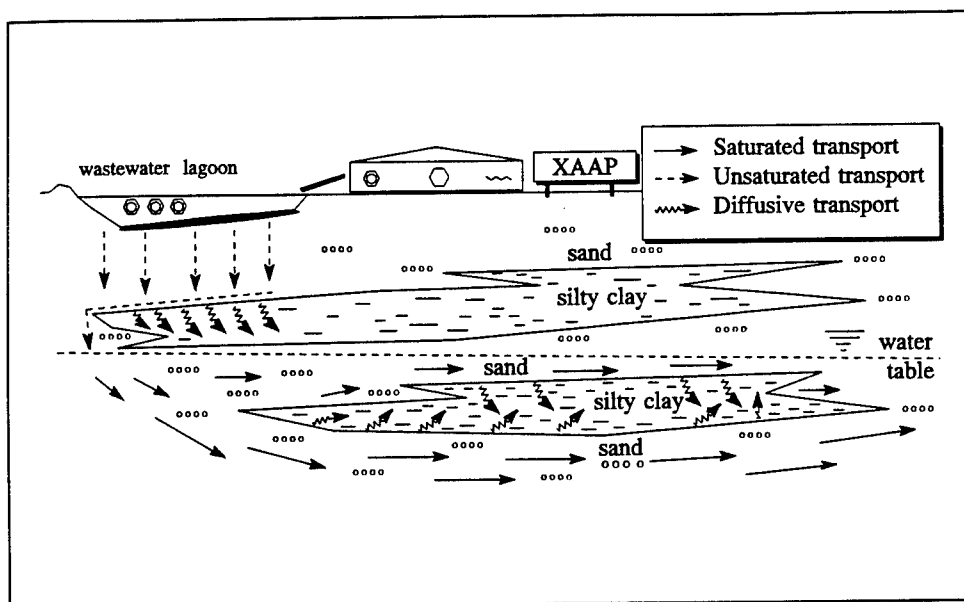
Figure 5.7. Schematic diagram of field-scale heterogeneities affecting
contaminant transport in porous media

Figure 5.5) or aggregate mesopores (Figure 5.6). Sorbate molecules also may
diffuse along the water-solid interface through a zone of adsorbed water (sur-
face diffusion; process 4 in Figure 5.5). Pore diffusion is generally faster
than surface diffusion in low tortuosity media (e.g., natural soils versus very
high tortuosity in activated carbon), assuming that steric hinderance is minimal
(Brusseau and Rao 1989a).

At the mesoscopic or aggregate scale, on the order of 1 mm - 1 m,
mobile–immobile region, mass exchange again may be regulated by molecular
diffusion (Figure 5.6). Smaller scale, pore diffusion phenomena may or may
not be considered explicitly in mesoscale modeling, depending upon the appli-
cation. At the macroscopic or field scale (Figure 5.7), large-scale heterogene-
ities (1 to 10's of meters) in sediment fabric and mineralogy resulting from
varied depositional and diagenetic processes affect another form of physical
nonequilibrium.

Numerical modeling of field-scale phenomena requires the scaling, or
averaging, of natural variability in properties and processes. Scaling of
parameters for deterministic models sacrifices information on parameter vari-
ability and, conversely, the effects of that variability on the processes of
interest.

The commonly observed disparity between sorption behavior observed in
short-term, bench-scale, batch tests and that calculated from field-scale obser-
vations suggests that batch tests measure sorption phenomenon at a scale that
is sometimes obscured by field-scale sorption (or other) processes. One
source of the disparity may be due to the difference in sorbate-sorbent contact
times—hours to days for batch experiments versus months to years for solute
plumes. Ball and Roberts (1991a,b) suggest that exposure times on the order

of 1,000 days are required to attain equilibrium uptake of tetrachloroethene (PCE) and tetrachlorobenzene (TeCB) into unpulvarized Borden sand. Pulverizing the sediment decreases diffusion distances and thus reduces the time to reach equilibrium to 20 days (TeCB) or 3 days (PCE). Pulverizing also alters the surface area and mineralogy that would naturally act as sorbents. These observations indicate a significant rate-limited phenomenon that may require a nonequilibrium modeling approach to describe (Ball, Curtis, and Roberts 1992, Ball and Roberts 1991b, Miller and Pedit 1992).

The significance of diffusive nonequilibrium sorption in the fate and transport of XACs has not been evaluated thoroughly. The few long-term sorption experiments involving TNT indicate that sorption equilibrium is attained at long exposure times—Spanggord et al. (1980a) estimate 240 days, Brannon, Jessup, and Rao (1992) estimate 180 days.

Modeling physical nonequilibria

Numerical modeling of contaminant transport necessarily involves an averaging of field-scale properties and processes into a continuum at the scale of discritization. Traditionally, the effects of physical heterogeneities are lumped implicitly into the dispersion coefficient. One approach to explicitly incorporate the effects of these ubiquitous heterogeneities is with multicontinua models, of which a bicontinuum conceptualization (mobile-immobile water) has been applied most commonly. Immobile water regions are described with sink/source terms in solute transport equations.

Most physical nonequilibrium models that also consider adsorption-desorption within a particular region treat it as an equilibrium process (van Genuchten and Wierenga 1976, Brusseau and Rao 1989a). This simplifying modeling assumption may be relaxed (e.g., the SOMIM model of Selim and Amacher (1988), discussed in Section 5.6).

Physical nonequilibrium sorption models differ primarily in the description of solute mass transfer between two (or more) physical regions. Broadly, these may be categorized into Fickian diffusion, first-order mass transfer, or effective dispersion. Fickian diffusion models prescribe a molecular diffusion mechanism in terms of a diffusion coefficient D [$L^2 \cdot T$-1] as described in Section 3.2. Solute distribution within an immobile-water region may be spatially variable and depends on region shape, volume, and interfacial area. Thus, an explicit geometry for the immobile regions is required. First-order models describe the mass transfer with an empirical, mass transfer coefficient, α [T^{-1}], assume homogeneous mixing in immobile regions, and do not require specification of immobile region geometry. Effective dispersion models lump the effect of immobile regions on solute transport into the dispersion coefficient, D_{eff} [$L^2 \cdot T^{-1}$].

Dimensionless parameters. Several dimensionless parameters have been developed as useful measures of the relative significance of various solute

transport processes. The Damköhler number ($\omega_I = k L / v$) is a ratio of diffusion to advection rates, which provides a quantitative indicator of nonequilibrium (Crittenden et al. 1986, Brusseau and Rao 1989a). Definition of the two Damköhler numbers is presented in Equation 5-5. Nonequilibrium would tend to be enhanced by higher advective velocity contrast, slower transfer coefficients and/or larger characteristic diffusion lengths (L).

Biot numbers are the ratios of mass transfer rates by film diffusion (as the Stanton number, St) to intraparticle diffusion via pores (as the pore-diffusion modulus, Ed_p) and surface film (surface-diffusion modulus, Ed_s):

$$B_s = \frac{St}{Ed_s} \qquad and \qquad B_p = \frac{St}{Ed_p} \tag{5-42}$$

where

$$St = \frac{film\ mass\ transfer}{advective\ transfer} = \frac{(1 - n_m)\,k_f L}{n_m\,v\,a}$$

$$Ed_p = \frac{micropore\ mass\ transfer}{advective\ transfer} = \frac{L\,D_p\,Dg_p}{a^2\,v}$$

$$Ed_s = \frac{surface\ mass\ transfer}{advective\ transfer} = \frac{L\,D_s\,Dg_s}{a^2\,v}$$

where k_f is the film mass transfer coefficient [$L \cdot T^{-1}$], a is the characteristic length (e.g., sphere radius), and the dimensionless Dg terms are solute distribution ratios for pore and intraparticle sorbate concentration relative to bulk water composition.

Film mass transfer is rate-limiting when the Biot numbers are less than approximately 0.5, while intra-aggregate mass transfer resistance is rate-limiting if either of the Biot numbers is greater than 30 (Crittenden et al. 1986, Brusseau and Rao 1989a). Both mechanisms are important for the intermediate range of Biot numbers.

Fickian diffusion models

Fickian diffusion models describe the mass transfer of solute as proportional to a diffusion coefficient, D [$L^2 \cdot T^{-1}$], and the local concentration gradient ($\partial C / \partial z$, where z is the position within the film, micropore, or macropore), as described in Equation 3-6. Fickian models have been invoked to describe molecular diffusion through films (transverse and laterally) and both micropores and macropores. Discerning which diffusive mechanism is rate-limiting in a given situation is difficult. The few codes that consider all three diffusive processes provide insights. The consensus seems to be that for

most cases, film diffusion limits early uptake, but the intra-aggregate diffusion is the rate-limiting process during most of the sorption process (Brusseau and Rao 1989a). Therefore, most physical nonequilibrium models that have been developed to date are of the pore-diffusion variety, neglecting or lumping in film and surface diffusion (e.g., van Genuchten and Wierenga 1976, Selim, Davidson, and Iskandar 1990). Diffusion across thin films also is an important process in several solute transport processes: sorbate diffusion across a hydrous boundary layer, nutrient diffusion in biofilms (Chapter 7), and volatilization across the air-water interface (Chapter 6).

Definition of the immobile region geometry or volume is not a simple task, and indeed this difficulty is the major drawback of the Fickian model approach. Not only are immobile region geometries difficult to measure, but immobile region volume fractions and mass transfer coefficients appear to be flow velocity-dependent (Nkedi-Kizza et al. 1982, Brusseau 1992).

Pore versus surface diffusion. Diffusion into particles or aggregates may proceed via micropores, through surface films, or through the solid sorbent itself (see Figure 5.5). The relative significance of pore versus surface diffusion has been evaluated with models that simulate both. Surface diffusion tends to dominate in sorbents with highly tortuous porosity, such as activated carbon. Natural sediment and soil solids have much lower tortuosities; thus pore diffusion is much less impeded and surface diffusion is relatively less significant. Sensitivity analyses by Crittenden et al. (1986) indicate that for near-linear isotherms, differentiation between pore and surface diffusion is not critical but may be more important for strongly nonlinear isotherm interactions.

An effective intra-aggregate diffusion coefficient (D_{im} or D_a) may be defined when both pore diffusion (D_P) and surface diffusion (D_S) are significant:

$$D_i = D_p + D_s K_p \frac{\rho_a}{n_a}$$

(5-43)

where subscripts p, s, and a refer to pore, surface, and aggregate parameters. If pore diffusion dominates, the Biot number ($B = B_p + B_s$) is independent of concentration, i.e., $B = k_f a / D_p$, whereas if surface-diffusion dominates, B is concentration-dependent, i.e., $B = k_f a\, n_a / D_s K_p \rho_a$ (Brusseau and Rao 1989a). Surface diffusion is also indicated if diffusion coefficients fitted to a dual-resistance model for a conservative tracer transport through a structured medium show the pore diffusion coefficient (D_p) is greater than the bulk or mobile water diffusion coefficient (D_b); this case suggests an additional intra-aggregate process which may be surface diffusion (Brusseau and Rao 1989a).

Miller and Weber film-pore model. Miller and Weber (1984, 1986) develop a dual-resistance, diffusive mass transfer model to describe diffusion

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across a boundary layer film and through aggregate mesopores. In spherical aggregates, the temporal variation in absorption is:

$$\frac{\partial S_{im}}{\partial t} = D_{im} \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial S}{\partial r} \right]$$

(5-44)

where D_{im} [$L^2 \cdot T^{-1}$] is the immobile region diffusion coefficient, and r is the distance from the center of the sphere of radius a. At the aggregate margin ($r = a$) where the equilibrium solute concentration is c_s, mass balance is described by:

$$k_f (C_m - c_s) = D_{im} \rho \frac{\partial S}{\partial r}$$

(5-45)

where k_f is the film mass transfer coefficient [$L \cdot T^{-1}$], subject to the condition $\partial S / \partial r = 0$ at $r = 0$.

Crittenden/Hutzler model. Crittenden et al. (1986) and Hutzler et al. (1986) develop a set of models which includes film transfer and both pore and surface diffusion (e.g., DFPSDM—a dispersed flow, pore and surface diffusion model). Mass balance for the immobile region is:

$$n_{im} \frac{\partial C_{im}}{\partial t} + \rho_{im} \frac{\partial S}{\partial t} = \left[\frac{D_p n_{im}}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial C_{im}}{\partial r} \right] \right]_{pore} +$$

$$\left[\frac{D_s \rho_a}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial S}{\partial r} \right] \right]_{surface}$$

(5-46)

Crittenden et al. (1986) performed sensitivity analyses for spherical aggregates and found that predictions are most sensitive to sorption model parameters (e.g., partition coefficient, Freundlich isotherm coefficients) and aggregate properties (radius and porosity). These parameters should be measured independently. Conversely, the model predictions were less sensitive to the dispersion coefficient (D) and film diffusion rate constant (k_f); therefore estimates of these parameters may be sufficient.

Roberts et al. (1987) apply the DFPSDM to miscible displacement experimental data of Nkedi-Kizza et al. (1982) for tritium and radiolabeled chloride

and calcium transport through a structured soil. Pore diffusion appeared to dominate. Surface, diffusive mass transfer played a minor role.

Miller and Pedit model. Miller and Pedit (1992) present a dual-resistance, film and pore diffusion model to describe desorption hysteresis of lindane sorption to spherical particles of radius a [L]. Mass balance expressions for mobile water concentration is described by:

$$\frac{\partial C}{\partial t} = -\frac{3 k_f M_S}{a V \rho} (C - C_S) - k_a C \tag{5-47}$$

where k_f is the boundary layer or film mass-transfer coefficient [L·T^{-1}], M_s is the mass of solid phase, V is the solution phase volume [L^3], and C_s is the equilibrium concentration at the solid surface. The sorbed mass balance is:

$$\frac{\partial s(r)}{\partial t} = D_S \left[\frac{\partial^2 S_r}{\partial r^2} + \frac{2}{r} \frac{\partial S_r}{\partial r} \right] - k_s S_r \tag{5-48}$$

subject to the following aggregate boundary conditions:

$$\frac{\partial s_r}{\partial r}\bigg|_{r=a} = \frac{k_f}{D_s \rho}(C - C_s) \quad (a)$$

$$\frac{\partial s}{\partial r}\bigg|_{r=0} = 0 \quad (b) \tag{5-49}$$

where r is the radial distance from the particle center, D_S is the intraparticle diffusion coefficient [L^2·T^{-1}], k_f is the boundary film transfer coefficient [L·T^{-1}], and ρ is the particle density. The initial condition, s_r ($0 \leq r \leq a$, $t=0$) $= 0$, and equilibrium partitioning at the solid surface described by a Freundlich model, $C_s = (s_{r(r=a)}/K_F)^{1/nf}$, are modeled. Pseudo first-order reaction models with rate constant k_a [T^{-1}] are adopted to describe degradation of solute (Equation 5-49) and sorbate (Equation 5-50).

Pore diffusion or multicontinua models

The simplest, and the most utilized, representation of hydrodynamic heterogeneity in porous media is as a bicontinuum of mobile and immobile water regions. Such dual-porosity models have been applied to solute transport in structured soils and fractured porous media. The bicontinuum conceptualization is an intuitive and appealing, deterministic approach for macroscale applications. Representation of strongly heterogeneous geologic media as a duality is still an oversimplification, but the approach is more realistic than assuming homogeneity.

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Soils develop cracks and burrows through which water and contaminants may flow preferentially (macropores). The (micro)porous, aggregated material between macropores is the matrix. The soil may develop a distinctive suite of matrix block shapes—granular, planar, blocky, or vertical columnar or prismatic (Hillel 1980). The sizes, shapes, and densities of these aggregate blocks vary within the soil profile.

Fickian diffusion models require input as to the geometry of immobile regions. Several analytical models have been developed for simple geometries (sphere, cylinder, plate) of uniform size. Models to accommodate mixed sizes and shapes have also been developed.

Spherical aggregates. The volume average concentration C_{im} within a spherical immobile water zone of radius b at time t is described by:

$$C_{im} = \frac{3}{b^3} \int_0^b r^2 C_a (r, x, y, z, t) \, dr \qquad (5\text{-}50)$$

where C_a is the local concentration in the aggregate at radial distance r (Goltz and Roberts 1986, Nkedi-Kizza et al. 1982). Fick's law for diffusion in a porous sphere with an aggregate retardation factor of R_{im} is:

$$R_{im} \frac{\partial C_a}{\partial t} = \frac{D_a}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial C_a}{\partial r} \right] \qquad (5\text{-}51)$$

where D_a is the effective diffusion coefficient [$L^2 \cdot T^{-1}$] for the aggregate matrix (Rao et al. 1980a, van Genuchten 1985). Wu and Gschwend (1986) also developed a radial diffusive penetration model to describe diffusion-limited adsorption kinetics for aggregate material.

Cylindrical aggregates. Volume averaged concentration in cylindrical aggregates of radius a and length z is described by:

$$C_{im}(z, t) = \frac{2}{a^2} \int_0^a r C_a (z, r, t) \, dr \qquad (5\text{-}52)$$

where C_a is the local concentration at radial distance r (van Genuchten 1985). Fick's law for mass transfer into a cylindrical aggregate is described by the cylindrical diffusion equation:

$$R_{im} \frac{\partial C_a}{\partial t} = \frac{D_a}{r} \frac{\partial}{\partial r} \left[r \frac{\partial C_a}{\partial r} \right] \qquad (0 \leq r \leq a) \qquad (5\text{-}53)$$

Platy and rectangular aggregates. Platy aggregates may be treated as either a plane of infinite lateral dimensions and thickness $2a$, or a rectangular or circular disk of thickness less than $2a$. The average concentration within a planar aggregate (line-sheet of van Genuchten (1985)) is:

$$C_{im}(z, t) = \frac{1}{a} \int_0^a C_a(z, x, t)\, dx \qquad (5\text{-}54)$$

where the coordinate x is normal to the plate surface. Linear diffusion within the immobile region is described by:

$$R_{im} \frac{\partial C_a}{\partial t} = D_a \frac{\partial^2 C_a}{\partial x^2} \qquad (5\text{-}55)$$

for $0 \le x \le a$.

Shape factors for Fickian diffusion models. Aggregates in natural soils and sediments typically contain a mixture of shapes and sizes. Analytical solutions are unavailable for many common shapes, such as cubic aggregates. van Genuchten (1985) defined empirical correlations between the mass transfer behavior of various shaped aggregates and spherical aggregates. By expressing irregular shaped aggregate behavior in spherical equivalents, a single model for spherical aggregates could be adjusted easily to accommodate disparate aggregate forms. Correlations are defined in nonflowing systems with four macropore-mesopore cases, for which analytical solutions were available —spherical, rectangular, and cylindrical aggregates, and large cylindrical macropores (van Genuchten 1985).

The empirical, shape factors are utilized to convert the characteristic length or key dimensionless parameters for a given aggregate type into a spherical aggregate with equivalent sorption behavior. van Genuchten (1985) defined a dimensionless parameter γ which contains the shape-unique parameters of characteristic length (a) and diffusion coefficient (D_a). The ratio of dimensionless parameters, solved for the spherical parameter, is:

$$\gamma_s = \frac{D_{im}\, \theta\, L}{f_{x,s}^2\, a_x^2\, q\, R_{im}} \qquad (5\text{-}56)$$

where D_{im} is the effective diffusion coefficient [$L^2 \cdot T^{-1}$], θ is the total water content, L is column length, $f_{s,x}$ is the shape factor to convert shape x into equivalent spheres, a_x is the characteristic length for the nonspherical aggregate, q is specific discharge, and R_{im} is the retardation factor for aggregate material. Table 5.6 lists a representative suite of shape factors (van Genuchten 1985).

Table 5.6 van Genuchten (1985) Shape Factors for Conversion of Nonspherical Aggregates Into Spherical Equivalents[1]					
Original Aggregate	Dimensions (x,y,z) or (2r,z)	Spherical Equivalent	Plane Sheet Equivalent	First-Order Equivalent	Comment
Sphere	2a	$f_{s,s}=1.000$	$f_{s,l}=0.394$	$f_{s,l}=0.210$	2a = diameter
Plane Sheet	2a,∞,∞	$f_{l,s}=2.54$	$f_{l,l}=1.0$	$f_{s,l}=0.533$	2a = thickness or width
Rectangular Prism	2a,2a,∞	$f_{r,s}=1.49$	$f_{r,l}=0.585$	$f_{r,l}=0.312$	square prism of infinite length
	2a,2a,8a	1.36	0.535	0.285	
	2a,2a,4a	1.24	0.490	0.261	
	2a,2a,2a	1.046	0.412	0.220	cube
	2a,2a,2a/8	0.279	0.110	0.0586	square plate
Solid Cylinder	2a,∞	$f_{c,s}=1.44$	$f_{c,l}=1.44$	$f_{c,l}=1.44$	2a = diameter
	2a,8a	1.32	0.521	0.277	
	2a,2a	1.030	0.406	0.216	
	2a,2a/8	0.279	0.110	0.0585	disk
First-Order Rate Model		$f_{l,s}=4.76$	$f_{l,l}=1.88$	$f_{l,l}=1.0$	

[1] Diffusion occurs along dimension x (sheet and prism aggregates) or r (spherical and cylindrical aggregates).

The spherical equivalent shape factors for cylindrical aggregates show a geometry-dependent variation with average matrix concentration. For rectangular, prismatic, cylindrical, and cubic aggregates the shape factors deviated by less than 10 percent from the shape factor at the average concentration ($0.5\ C_o$). Variation was more severe for planar aggregates.

Mixed shape and size aggregates. Natural aggregates form in a range of sizes, shapes, and porosities. Multiple aggregate porosities and shapes could be modeled as multimodal distribution. A few schemes for weighted averaging of mixtures of aggregate types have been proposed, primarily in the chemical engineering literature (e.g., Rasmuson 1985); these are briefly reviewed by Brusseau and Rao (1989a, p. 53). Rao et al. (1982) established that mixtures of cubic and spherical aggregates of varying size could be represented by a volume-weighted average of a single spherical aggregate size. The cubic aggregates could be represented with equivalent spherical forms of the same volume. Brusseau and Rao (1989a) suggest that single-aggregate models are probably adequate for most soils and aquifer material.

First-order mass transfer models

First-order mass transfer models describe the diffusion process in terms of a linear, chemical gradient between mobile and immobile regions and a first-order rate coefficient, α [T^{-1}]. Concentrations in both regions of the bicontinuum are volume-averaged (homogenized), i.e., there are no intra-aggregate or intraparticle diffusion gradients. Thus, the first-order model is much simpler than the Fickian model in that aggregate geometry needs not be specified.

van Genuchten and Wierenga (1976, 1977) presented a model to describe physical nonequilibrium of solute transport through unsaturated aggregated soil, utilizing the first-order, or α-, approach. For sorption, fitting a nonlinear, Freundlich isotherm (or $\partial S / \partial t = K_F \, b_F \, C^{b_F - 1} \, \partial C / \partial t$), the advection-dispersion equation becomes:

$$\theta_m R_m \frac{\partial C_m}{\partial t} + \theta_{im} R_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D \frac{\partial^2 C_m}{\partial x^2} - \theta_m V_m \frac{\partial C_m}{\partial x} \quad (5\text{-}57)$$

where the Freundlich-based retardation factors are defined for the mobile (R_m) and immobile (R_{im}) regions as:

$$R_m = 1 + f \, \rho_b \, K_F \, b_F \, C_m^{(b_F - 1)} / \theta_m \qquad (a)$$
$$R_{im} = 1 + (1 - f) \, \rho_b \, K_F \, b_F \, C_{im}^{(b_F - 1)} / \theta_{im} \qquad (b)$$

$$(5\text{-}58)$$

The θ terms are moisture contents of the two regions ($L^3 \cdot L^{-3}$; $\theta = n_T$ at saturation); the subscripts refer to mobile (m) and immobile (im) regions. The C term is the aqueous concentration [$M \cdot L^{-3}$]. In the mobile water region, D is the dispersion coefficient [$L^2 \cdot T^{-1}$], and v is seepage velocity [$L \cdot T^{-1}$]. The mass transfer between regions is:

$$\left[\theta_{im} + (1-f)\rho_b \, K_F \, b_F \, C_{im}^{(b_F - 1)} \right] \frac{\partial C_{im}}{\partial t} = \alpha \, (c_m - c_{im}) \quad (5\text{-}59)$$

where α is the first-order rate coefficient [T^{-1}].

For linear and reversible sorption ($b_F = 1$), the van Genuchten and Wierenga model reduces to:

$$\left[\theta_m + f \, \rho_b \, K_d \right] \frac{\partial C_m}{\partial t} + \left[\theta_{im} + (1-f)\rho_b \, K_d \right] \frac{\partial C_{im}}{\partial t}$$
$$= \theta_m D \frac{\partial^2 C_m}{\partial x^2} - \theta_m v_m \frac{\partial C_m}{\partial x}$$

$$(5\text{-}60)$$

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and the mobile-immobile region mass transfer is:

$$\theta_{im} R_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im})$$

(5-61)

where R_{im} is described by a linear Freunlich isotherm—Equation (5-58b) for $b_F = 1$. van Genuchten and Wierenga (1976) derive an analytical solution to this latter expression for pulse transport through a semi-infinite column of aggregated, porous material.

Although the mass transfer coefficient, α, often is described as an empirical parameter, further analysis indicates that it depends on the aggregate size, and diffusion coefficient, as well as on flow velocity (van Genuchten and Wierenga 1977, De Smedt and Wierenga 1984). Raats (1981) related α to sorption parameters for sheet and spherical aggregates and noted that:

$$\alpha_{sheet} = \frac{3 D_a}{4 a^2} \quad and \quad \alpha_{sphere} = \frac{15 D_a}{a^2}$$

(5-62)

Parker and Valocchi (1986) determined a similar expression for the sphere, including a factor of θ_{im} in the numerator.

van Genuchten (1985) also established correlations for spherical equivalents to the first-order model approach (see Table 5.6). The transfer coefficient may be related to the shape factor by:

$$\alpha = \frac{D_{im} \theta_{im}}{f_{s,x}^2 a_x^2}$$

(5-63)

The transformation to an "equivalent first-order rate model" was not as accurate as analogous transformation to spherical equivalent Fickian diffusion models described above. However, the accuracy was described as "probably good enough" for field application in light of the many parameter uncertainties in two-region models to justify use of the simpler first-order model.

Effective diffusion models

Nonequilibrium mass transfer between mobile and immobile regions tends to increase observed dispersion. Effective dispersion models lump implicitly the influence of immobile regions into an effective dispersion coefficient, D_{eff}. The key assumption is that solute residence times are sufficient to achieve minimal concentration gradients between mobile and immobile regions (a variation on the LEA theme).

Parker and Valocchi (1986) described the effective dispersion coefficient model in terms of spherical diffusion models. For a sorbing solute, the effective dispersion coefficient is described by:

$$D_{Eff} = \phi D_m + \frac{(1-\phi) a^2 v^2 R_{im}^2}{15 D_a [\phi R_m + (1-\phi)R_{im}]^2}$$
(5-64)

where ϕ is the fraction of mobile water (θ_m/θ), and a is the aggregate radius. For conservative solutes ($R_m = R_{im} = 1$), Equation 5-61 reduces to:

$$D_{Eff} = \phi D_m + \frac{(1-\phi) a^2 v^2}{15 D_a}$$
(5-65)

which is equivalent to those derived by Passioura (1971) and Raats (1984).

The effective dispersion has been observed to be 5-20 times that of D estimated without consideration of physical nonequilibrium processes (Brusseau and Rao 1989a). As with field-determined dispersion factors, the effective coefficient appears to stabilize at large travel distances or times. Fair agreement between observed and predicted solute transport has been reported as long as $(1-\phi)D_{eff}L/(v a^2) > 0.3$ (Rao et al. 1980a).

Intrasorbent diffusion

Solutes may diffuse into the structure of minerals and organic solids. Intramineral diffusion is conceivable for microporous minerals such as expandable clay minerals (interlamellar space) and zeolites (highly porous tectosilicates; "molecular sieves"). Soil organic matter may be conceptualized as a microporous, three-dimensional matrix of polymer chains; soil humic material may be characterized as a membrane-like aggregate (Wershaw 1986, 1992, 1993, Sposito 1986). Soil organics appear to play a significant role as an permeable sorbent, particularly for hydrophobic solutes. Steric hindrances may occlude large organic solute molecules from intramineral regions. This fact is consistent with observations for pesticide sorption to inorganic materials which showed time-independence versus the delayed approach to equilibrium observed for organic-rich soils (Brusseau and Rao 1989a). Internally adsorbed molecules may also become trapped if sorbent penetrability is subject to reduction (e.g., collapsing clays, desiccated organic matter) in response to hydrogeochemical conditions.

Brusseau and Rao (1989a,b) and Brusseau, Jessup, and Rao (1991) suggest that the rate-limited mass transfer of hydrophobic organic compounds (HOCs) into soil organic matter is a likely contributor to nonequilibrium transport, distinct from the strictly physical and chemical processes described above.

(IOMD) would be equivalent to the descriptors reviewed above. Only the physical conceptualization of parameters would change; for example, the immobile region would now be the organic matrix.

Experimental evidence in support of the IOMD concept (Brusseau and Rao 1989a) include reports that HOC:

a. Sorption/desorption rates decrease with increasing organic matter content (Karickhoff 1980).

b. Sorption/desorption rates decrease with increasing K_{oc} or K_p (Karickhoff and Morris 1985, Brusseau and Rao 1989b).

c. Sorption/desorption rates increase in presence of miscible cosolvent (Nkedi-Kizza et al. 1989).

d. Sorption nonsingularity increases with increasing soil organic matter content and with solute K_{oc}.

e. Sorption nonequilibrium increases with sorbent organic matter content and hydrophobicity (Bouchard et al. 1988).

An IOMD model should be considered with other alternatives when a sorbing, hydrophobic solute shows an asymmetrical BTC and a conservative cosolute does not.

The inverse relation between partitioning (K_p) and sorption kinetics (k) has been described quantitatively for 61 HOCs as:

$$\log k = 0.301 - 0.668 \log K_p \quad\quad (5\text{-}66)$$

with an r^2 of 0.95 (Brusseau and Rao 1989b). This observation is consistent with suggestions that more hydrophobic solutes require much longer times (weeks to months) to attain an equilibrium condition, and that this delay is diffusion controlled. A similar analysis of 12 polar or ionizable organic compounds indicated a different linear relation which was less well-correlated ($r^2 = 0.4$): $\log k = -1.789 - 0.62 \log K_p$. The solute polarity likely introduces other possible sorption mechanisms which add to the data scatter.

Descriptors for intraorganic diffusion of HOCs (negligible chemisorption) could be similar in form to the intra-agregate sorption models—Fickian diffusion, first-order mass transfer, or effective dispersion. The IOMD concept may act simultaneously with intra-aggregate diffusion, which may account for additional kinetic processes suggested by the occasional inadequacy of simpler bicontinuum models. An IOMD mechanism could be added in series or in parallel to a two-region model.

5.6 Hybrid Nonequilibrium Models

Combining multicontinua physical and multisite chemical kinetics features into a single model is appealing, at least in terms of conceptual flexibility. Few attempts have been made to produce such a code (Selim and Amacher 1988, Selim, Davidson, and Iskandar 1990).

Experiments by Nkedi-Kizza et al. (1984) and van Genuchten and Wagenet (1989) demonstrate that, for linear isotherms, two-site and two-region models expressed in dimensionless parameters may reproduce observations equally well, and indeed are mathematically identical. They show that interpretation of breakthrough curve data alone does not yield unique solutions to the two-site or two-region model. Physical and chemical nonequilibrium cannot be differentiated.

Selim and Amacher (1988) and Selim, Davidson, and Iskandar (1990) develop and evaluate several two-site kinetic models with and without a two-region feature. Chemical kinetics are modeled by specifying first-order rate constants for each forward and reverse sorption. Selim and Amacher (1988) include two rate-limited reaction sites, whereas the Selim, Davidson, and Iskandar (1990) models also included equilibrium sites, a third rate-limited site in parallel with another kinetic site, and irreversible reaction kinetics. Physical nonequilibrium is treated with both a first-order mass transfer model and a second-order model (first order in both solute concentration and sorbent site availability).

5.7 Comparison of Modeling Approaches

Physical nonequilibrium models. Comparisons of the three nonequilibrium models (Fickian diffusion, first-order mass transfer, effective dispersion) suggest that only marginal improvement is gained by applying the more complex diffusion model versus the mass transfer model approach (Rao et al. 1980b, Parker and Valocchi 1986, Goltz and Roberts 1986, Brusseau and Rao 1989a). Parker and Valocchi (1986) suggest further that little is gained by using a mass transfer model over an effective dispersion model, at least for spherical geometries. Some of the key attributes of these modeling approaches are summarized in Table 5.7.

It may be that nonequilibrium processes operative and resolvable at the bench scale are not important relative to other processes at the field scale. Yet, most process characterization is conducted at the bench scale. The microscale processes must be identified and quantitated in order to interpret results of experiments in which multiple processes are ongoing simultaneously.

Table 5.7
Summary of Physical Nonequilibrium Sorption Models Attributes

Model	Assets	Liabilities
Fickian	Conceptually most correct and flexible.	Requires aggregate geometry and diffusion parameters.
First-Order	Comparable results to Fickian with much less difficulty. Optimal balance of complexity and accuracy.	Loss of reliablility above critical velocity threshold.
Effective Dispersion	Simple.	Least conceptually correct for heterogeneous media.
Intraorganic Matter Diffusion	High applicability to HOCs.	May not be strictly applicable to XACs.

Which physical nonequilibrium models are most appropriate for field-scale applications is uncertain. The physical, nonequilibrium processes important at the pore scale (e.g., intraparticle diffusion) appear to be overshadowed in the field by larger scale intrastratum diffusion. Analyses by Wilson (1992) and others indicate that because the diffusion length scale for field-scale heterogeneities is great relative to intraparticle diffusion, the heterogeneities are largely responsible for the failure of pump-and-treat as a remediation technology.

Comparison of nonequilibrium models. Each of the reviewed approaches to modeling nonequilibrium sorption phenomena has certain advantages and disadvantages. The recommended approach is to apply two or three different models, consistent with available information and experimental data. Although this approach may not be practical for every application, it is preferable for research level of process investigations. A multiple working model approach may provide additional insights as to sorption mechanisms and avert model myopia.

Distinguishing chemical and physical processes in natural media is difficult because they proceed simultaneously. Independent estimates under controlled experimental conditions are required, though not typically practical. Some guidelines are available, however, to implicate a mechanism type (see Table 5.8). For example, rate coefficients for physical nonequilibrium processes tend to be sensitive to flow velocity, mixing rate, and particle or aggregate size and structure but are not affected strongly by temperature. Chemical kinetic processes tend to be strongly affected by temperature variation but not sensitive to flow velocities and aggregate structure (Brusseau and Rao 1989a).

5.8 Sorption Singularity or Hysteresis

As introduced earlier, sorption/desorption nonsingularity, or sorption hysteresis, is one of several potential sources of sorption nonideality (Brusseau

Table 5.8
Summary of Processes to Which Alternative Nonequilibrium Sorption Models Attribute Observed Phenomena[1]

	Observed Phenomena or Feature		
	Rate-limiting Process	Early Breakthrough	BTC Tailing
Chemical (Section 5.4)	"Slow" kinetics sites or sorbents versus rapid sites	Solute escapes influence of nonequilibrium process(es)	Slow desorption from slow sites
Physical (Section 5.5)	Diffusive mass transfer between mobile and immobile zones	Advective transport via high-mobility zones, $q/\theta_m > q/\theta$	Diffusion out of immobile regions
Intraorganic Diffusion (Section 5.4)	Partitioning and diffusion into/out of organic matter	Advective, solute bypass of organics	Diffusion out of organic matter

[1] After Brusseau and Rao (1989a).

and Rao 1989a,b). Adsorption and desorption isotherms are singular (nonhysteretic) if they are coincident, and nonsingular (hysteretic) if significant deviation is observed. Numerous reports of disparate desorption and adsorption isotherms are reported (e.g., DiToro 1985). The source of such hysteretic behavior may be real or an experimental artifact, and it is not easy to distinguish from literature reports. True nonsingular behavior may arise from the following:

a. *Chemical or biological reactions.* Such reactions may alter the adsorbate and increase its partitioning behavior.

b. *Chemisorption or covalent bonding to sorbent surface.* Specific interactions involving strong, covalent bonding between sorbate and sorbent constituents may bind adsorbates irreversibly.

c. *Physical entrapment within the sorbent.* Certain sorbents expand and contract in response to chemical or environmental conditions (e.g., swelling clays, organic solids). Solutes may be physically trapped if solutes adsorb to opened structures, and then conditions change to induce constriction of the micropores.

Conversely, apparent nonsingularity may arise from the following:

a. *Failure to attain true adsorption or desorption equilibrium.* For example, if a desorption experiment is begun before sorption is complete, or stopped before desorption equilibrium is attained, isotherm disparity may be misinterpreted as nonsingularity. Solute may still be diffusing

toward interior of an aggregate or organic matter even after desorption is initiated (Brusseau and Rao 1989a).

b. *Experimental artifacts.* Brusseau and Rao (1989a) cite the example of desorption experiment conducted by a successive dilution that involves agitation to resuspend solids. It appears that this agitation may break up soil aggregates or particles, thereby exposing new, previously unoccupied surfaces or sites and impeding desorption. Conversely, desorption could be enhanced if particle breakup reduces the diffusion path length out of the particle.)

c. *Artifact of sorption "measure"-by-difference method.* Unaccounted for losses attributed erroneously to partitioning or diffusion to the sorbent may be the result of abiotic or biotic transformations, solute loss by volatilization or sorption to container walls, and sorption to organics colloids or cosolutes which may or may not be separated prior to aqueous phase extraction. Transformation or complexation products may possess different partitioning behavior, which can enhance or inhibit adsorption.

d. *Artifact of competitive sorption phenomenon.* If sorption sites are initially occupied, e.g., by the implicit adsorbate of Curl and Keoleian (1984), sequential, batch adsorption, and desorption procedures may remove the implicit adsorbate, which will enhance the partitioning of the explicit solute by making more sites available.

Many reports of irreversible sorption or hysteresis may be the result of physical nonequilibrium processes. Evidence of diffusion-based hysteresis may be: (a) long-term resistance to desorption, with no evidence of irreversible binding, (b) an increase in the resistant component with time of exposure, i.e., solute has more time to diffuse into immobile zones, and (c) if several sorbates with typically disparate sorptive mechanisms appear to be affected in the same way, as described above. Desorption from aggregate material not at equilibrium should be expected to take longer than adsorption since even if loading is ceased, solutes will continue to diffuse toward aggregate centers before the concentration gradient is completely reversed in favor of desorption.

Most models neglect sorption hysteresis on the assumption that other nonequilibrium phenomena are much more influential in solute transport. If hysteresis is to be modeled, sorption and desorption isotherms must be measured.

5.9 Cosolvent Effects on Sorption

The presence of multiple organic species in soils or aquifers can enhance aqueous solubility (synergistic cosolvency) or increase its retardation

(antagonistic cosolvency). Numerous cosolvency effects have been documented experimentally and/or estimated based on liquid-liquid equilibrium models.

In situ cosolvent flooding has been implemented or proposed as a remediation technology in the cleanup of nonaqueous phase liquids and strongly sorbed organics (Augustijn et al. 1992). The effect of hydrophilic cosolvents such as alcohols to enhance the aqueous solubility of hydrophobic organics partitioning is well-demonstrated (Kan and Tomson 1986, Kan, Tomson, and McRae 1992, Brusseau, Wood, and Rao 1991, Groves and El-Zoobi 1990, Nkedi-Kizza, Rao, and Hornsby 1985, 1987, Palmer and Fish 1992).

Brusseau (1991b) and others have shown that the presence of relatively hydrophobic cosolutes increases the retardation of more soluble organics. Brown et al. (1992) and Hatfield et al. (1992) have suggested that the emplacement of a cationic surfactant on low organic carbon, aquifer material across the path of an HOC solute plume would create a sorption curtain or wall onto which HOCs would partition. The enhanced retardation could be utilized to slow plume migration and allow slower processes, such as anaerobic biodegradation to be effective in solute degradation.

Desorption and enhanced transport of XACs by cosolvents is likely to occur in field settings and thus may require characterization for accurate predictive modeling. However, enhanced transport as a remediation technology is not likely to be cost-effective due to the relatively low partitioning of most XACs. Surfactant or cosolvent flooding has been proposed for the remediation of strongly hydrophobic organic contaminants. Enhanced retardation for plume management is an interesting technology, but until the sorption and other reaction mechanisms affecting XACs are better defined, this technology will remain in the research stage.

5.10 Research Recommendations

Sorption of XACs is far from well understood. A general sense for which soil components are important in the sorption of explosives has evolved out of statistical analyses relating sorptive behavior to soil properties (Pennington 1988, Ainsworth et al. 1993). These analyses have implicated certain soil components as being involved in, or at least correlated to, XAC sorption. Correlations do not establish reaction mechanisms. However, correlations can suggest specific sorption mechanisms worthy of closer scrutiny. A more complete understanding of specific sorption reactions is needed to move beyond empirical curve-fitting to develop truly predictive fate and transport models. Sorption behavior of the transformation products of explosives is much less well established. Virtually any research, experimental or theoretical, would be valuable in filling these data gaps.

Most of the sorption descriptors reviewed here are applicable to XACs as well as other solutes. Models based on hydrophobic partitioning may be useful for certain XACs (e.g., RDX) but not others; the same is true for specific interaction models. Physical nonequilibrium models are applicable to any solute. Investigations are needed to assess XAC sorption processes and appropriate descriptors at multiple levels—from improving understanding of specific molecular interactions, to the significance of media heterogeneities on XAC transport at all physical scales. Following is a collection of recommendations for consideration for further investigations of XAC sorption.

Establish the dominant sorption mechanisms affecting XACs transport. Certainly the most fundamental gap in the understanding of nitroaromatic contaminant sorption is the limited knowledge of the specific sorption reactions common in natural soils and aquifer material. Numerous indications and correlations of sorption behavior to soil parameters, such as iron content, hint at sorption mechanisms, but these remain speculative. A series of experiments with thoroughly characterized or homogeneous (one- or two-site type) sorbents would provide stronger evidence for or against specific interactions. Evaluation of similar nitroaromatic compound in homologous series provides further indication as to what specific interactions are active. For example, TNT sorption mechanisms may be elucidated if consistent trends are observed in the sorption of dinitrotoluene(s), nitrotoluene(s), toluene, and benzene (and perhaps analogous cycloalkanes) in the same sorbent system.

Evaluate correlation to soil organic functional groups. The relatively weak correlation between TNT sorption and the fraction of organic carbon (f_{oc}) in natural soils has raised questions as to the role of hydrophobic partitioning for XACs. Contaminants with polar and/or reactive functional groups (most XACs) are more likely to be involved in specific sorption reactions. The specific nature of the soil organics functional groups may be a more relevant measure than bulk content, f_{oc}. Two possible approaches to assessing the influence of structural components follow: (a) evaluate XAC sorption onto organic or synthetic sorbents for which the surface chemistry is known and uniform; and (b) evaluate XAC sorption to heterogeneous, natural organic sorbents for which the structural chemistry has been at least semiquantitatively characterized in terms of functional group moieties. Perhaps soil organic functional groups may be identified quantitatively by IR or NMR spectroscopy.

Evaluate the sorption mechanism involving extractable iron. How "extractable iron" facilitates TNT sorption is uncertain. To elucidate the role of iron in XAC sorption, a more detailed characterization of the Fe content is necessary. What is the crystalline state of Fe solids (amorphous versus crystalline; mineralogy), or is the significant iron form an adsorbed ion or complex? The suggested role of Fe^{2+} sorbates involved in a water-bridge mechanism merits further investigation. Perhaps evaluation of possible formation of aqueous metal-XAC complexes would contribute to the question of whether such complexes form at surfaces. Comparison of Fe^{2+} to other

metals, such as Mg^{2+} which has more tightly bound hydration layer, may also shed light on the suggested water-bridge sorption mechanism.

Evaluate the influence of clay mineralogy. As with bulk f_{oc}, a bulk clay content, particularly one based on particle size data, is not very enlightening beyond a crude indicator of surface area. Only weak inference of composition is possible from particle-size analyses. A more useful measure would be a quantitative determination of clay mineralogy by X-ray diffraction, particularly the expandable clays. Clays are likely to contribute to sorption reactions, perhaps partially irreversible, with XACs.

Conduct both kinetic and equilibrium batch experiments. Both batch sorption rate and batch isotherm must be determined (MacIntyre et al. 1991). It must be established that equilibrium is attained and the minimum time required. If equilibrium is not attained reasonably quickly, the K_d concept is inappropriate and nonequilibrium models must be invoked. Experimental design should include very long-term exposures (months) to test intraparticle or intra-aggregate diffusion models. Isotherm experiments should be designed to evaluate sorption hysteresis. Careful statistical design should include replicate analyses on multiple soils/aquifer material from region to be modeled. Some indication of spatial variability in sorption behavior and a quantitative measure of experimental error is useful in sensitivity analysis, model calibration, and interpretation of model predictions.

Conduct column experiments in homogenized and structured media. To assess the importance of physical nonequilibrium processes and their descriptors, conduct a series of experiments in porous media with engineered heterogeneities of known geometry and character, and/or undisturbed cores or monoliths. Experiments on homogenized material serve to characterize bulk or possible intraparticle phenomena and establish a basis for evaluation of the effects of heterogeneities in structured soils. Noninvasive observation of solute transport in structured soils is a difficult challenge. Perhaps X-ray computed tomography (CT), magnetic resonance imaging (MRI), or in situ spectroscopy by chemical shift imaging (CSI) may be applied. There is a need to evaluate aquifer material at the microscopic level by porosimetry to determine pore size distribution, surface area (BET) etc.

Include multiple solutes in breakthrough experiments. At least one set of breakthrough experiments should include: (a) one or more XACs, preferably the parent compounds, (b) a conservative tracer such as tritium or chloride to evaluate dispersion, and (c) one or more simple organic solutes (e.g., nitrobenzene, aniline, toluidine) to serve as a reference for XAC behavior and experiment cross-comparison. Multiple constituents may require analysis by a chromatographic method, perhaps with tandem other detectors (e.g., HPLC and liquid scintillation). Experiments in structured, heterogeneous media should include solutes with widely ranging sorptive behavior.

Evaluate impact of environmental variables. Sorption experiments should be designed to assess the influence of various processes and conditions

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including competitive sorption (multiple-XACs), temperature, pH, Eh, and ionic strength. A solute concentration range sufficiently broad (from the detection limit to the solubility limit) would be preferable to detect nonlinearity, though emphasis is usually given to the expected range of solute concentrations.

Investigate QSPRs for property estimation. Quantitative Structure-Property Relations provide a cost-effective means by which to estimate environmental behavior of poorly characterized organic solutes (e.g., a great number of XACs). Properties or parameters for poorly known XACs may be estimated based upon empirical relations developed from observations of well-characterized compounds for which similar behavior is expected. K_{oc}-$K_{o/w}$-S correlations exclusively for nitroaromatics or nitrogen heterocyclics are not available and should be investigated.

6   Volatilization

Explosives associated contaminants (XACs) in unsaturated media will partition among all phases (or compartments) present, including: (a) the crystalline or noncrystalline XAC solid phase(s), (b) the aqueous phase as solutes, (c) the non-XAC solid phases as an adsorbate, and (d) the vapor phase (see Figures 6.1 and 6.2). A general definition of volatilization would include any mass transfer to the vapor phase from any other solid or aqueous phase. Processes and descriptors for vapor-solid and vapor-solute mass transfer are reviewed in this chapter. Volatilization of adsorbed XACs is not discussed explicitly, but descriptors would be very similar to those discussed for sorption in Chapter 5.

Volatilization of the common explosives (e.g., TNT, RDX, HMX) generally is considered to be negligible relative to other transport mechanisms (Spanggord et al. 1980a,b; Rosenblatt et al. 1989). The topic is reviewed for several reasons:

- Any decision to neglect volatilization in transport modeling must be justified.

- Volatilization may be important in the transport of several, lower molecular weight XACs, e.g., nitrobenzene.

- Air-water mass transfer and vapor transport processes may be crucial in modeling the transport of reactants and/or reaction products, e.g., O_2 and CO_2 in aerobic bioreactions.

- Volatilization of even the larger molecular weight XACs may be significant when viewed over a long time frame (decades).

Two fundamental processes involved in volatilization and vapor transport are reviewed in this chapter: (a) interphase mass transfer to the vapor phase from crystalline XAC solids (Section 6.1) or aqueous phase solutes (Section 6.2), and (b) advective, dispersive, and/or diffusive transport in the vapor phase through the porous media (Section 6.3). Adsorption directly from the vapor phase is not discussed; this process may be important in arid environments where soil water saturation is very low.
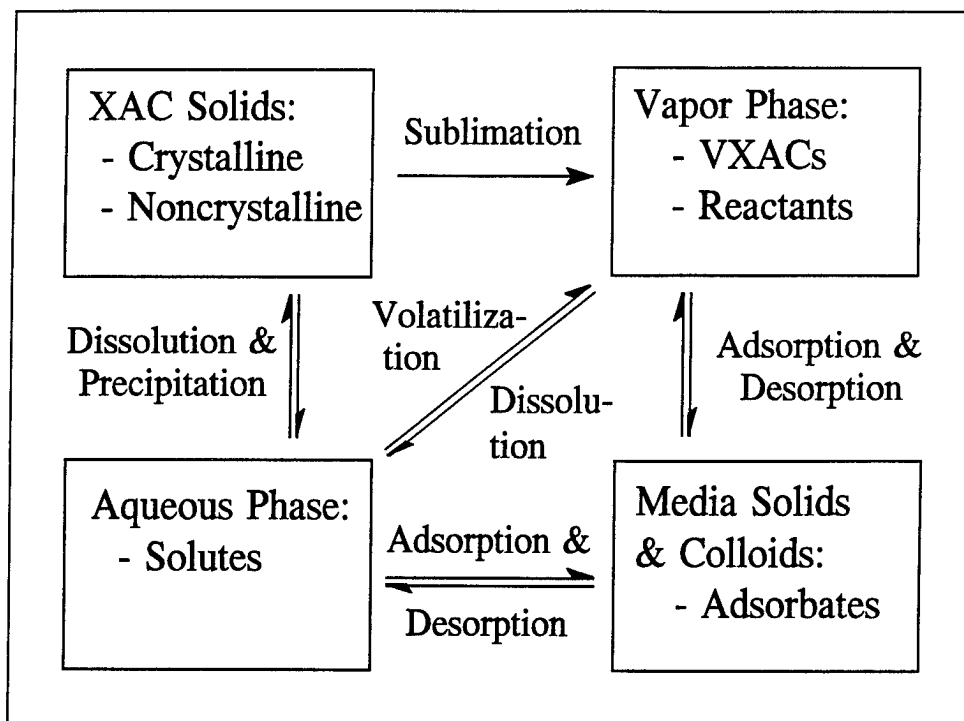
Figure 6.1. Schematic of mass transfer paths involving the vapor phase in unsaturated media
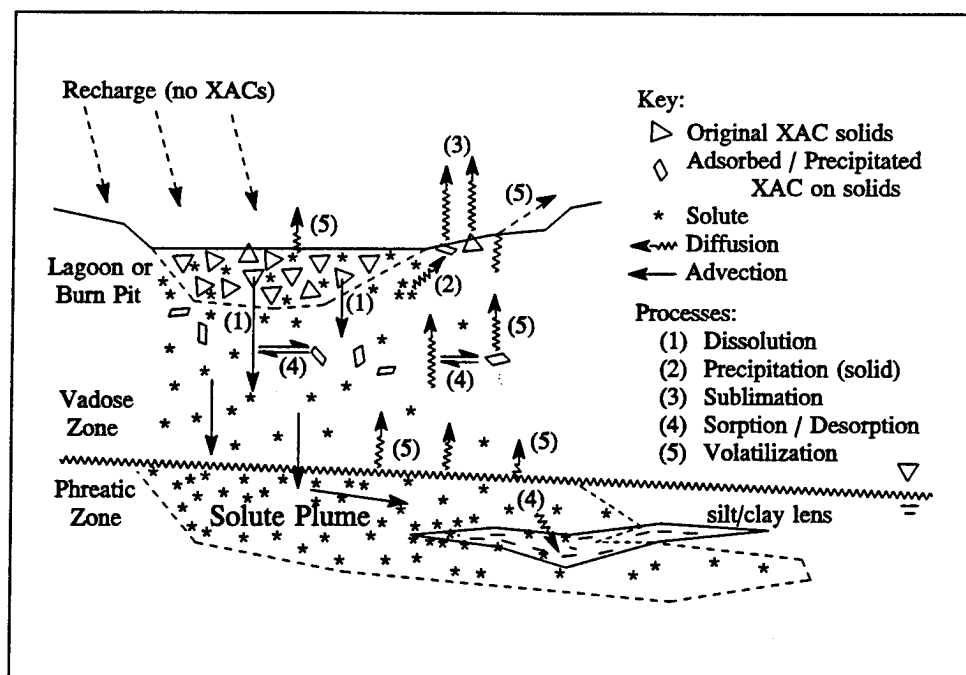
Figure 6.2. Schematic of subsurface depicting potential sources of mass transfer to the vapor phase

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Volatilization is typically discounted as a significant environmental pathway for common explosives because of their very low vapor pressure, P_v, and Henry's constant, k_H or K_H (see Table 6.1, Figure 6.4, and Appendix A). The vapor pressure of a solid (or liquid) is the pressure in the gas phase at equilibrium with the solid in a closed system at a specified, constant temperature. More volatile compounds have greater vapor pressures. Vapor pressures for sparingly volatile solids are difficult to measure accurately because of instrument sensitivity limitations and are thus subject to significant experimental error. Vapor pressures for most XACs have not been measured at environmental temperatures but rather are estimated by extrapolation from higher temperature observations employing an equation of state, or by an empirical correlation developed for similar compounds (Thomas 1990a).

6.1 Sublimation

Sublimation is the mass transfer from the solid phase directly to the vapor phase. The solid phase may be crystalline or noncrystalline; the degree of crystallinity would likely affect the rate of mass transfer inversely. Vapor pressure (P_v) is the equilibrium partial pressure (atm, torr, or Pa) of the compound in equilibrium with the pure solid or a saturated aqueous solution. P_v is a good indicator of the tendency of the material to sublimate.

Sublimation may be a pseudo first-order kinetic process, by analogy to aqueous dissolution (Section 4.2; Equation 4-15), assuming that diffusion away from the solid-vapor interface is not rate-limiting and the precipitation rate is negligible:

$$\frac{\partial C_{x\,(A)}}{\partial t} = k_s\,A_s\,C^o_{S\,x\,(A)} \qquad (6\text{-}1)$$

where $C_{x(A)}$ is the concentration of sublimating XAC in the air phase [$M\cdot L^{-3}$], k_s is the sublimation rate coefficient [$L^{-2}\cdot T^{-1}$], A_s is the XAC surface area, and $C^o_{Sx(A)}$ is the vapor solubility of compound x at equilibrium with pure compound (superscript o). As with aqueous dissolution, the sublimation rate is also dependent on the mass present and its surface area to volume ratio. To enter the vapor phase, molecules must overcome intermolecular forces within the crystalline structure. XAC solids may be pure or multicomponent, crystalline or amorphous; these conditions affect the volatility as well as solubility. To properly assess sublimation kinetics, the crystallinity and purity of the solid must be determined.

The Clausius-Clapeyron equations describe the dependence of P_v (atm) on temperature (T in degrees Kelvin; K = 273.15 + °C) and enthalpy change per mole (ΔH_v, cal·mol^{-1}; or heat of vaporization):

Table 6.1
Vapor Pressure, Aqueous Solubility, and Henry's Law Constant (Equation 6.5) for Representative XACs and Reference Compounds[1]

Compound[2,3]	Vapor Pressure, P_v (atm, 25°C)		Aqueous Solubility, C_S (mol $\cdot$ m^{-3})		Henry's Law Constant, k_H (atm $\cdot$ m^3 $\cdot$ mol^{-1})	
Explosives[R]	P_v	log P_v	C_S	log C_S	k_H	log k_H
TNT	7.25 E-09 →	- 8.140	6.604 E-01 →	-0.180	1.1 E-08 →	- 7.959
RDX	5.30 E-12 →	- 11.28	2.701 E-01 →	-0.569	1.96 E-11 →	- 10.71
HMX	4.38 E-17 →	-16.36	1.688 E-02 →	-1.773	2.6 E-15 →	- 14.59
XACs & homologous series:						
Benzene[V] (B)	≤ 1.28 E-01 →	- 0.894	2.872 E+01 →	1.458	4.45 E-03 →	- 2.352
Nitrobenzene[V] (nB)	3.29 E-04 →	- 3.483	1.956 E+01 →	1.291	1.68 E-05 →	- 4.774
1,3-dinitro-benzene[V](dnB)	2.54 E-07 →	- 6.595	3.17 E+00 →	0.501	8.01 E-08 →	- 7.096
trinitro-benzene[R] (tnB)	3.99 E-09 →	- 8.399	1.81 E+00 →	0.257	2.21 E-09 →	- 8.656
Toluene[V] (T)	≤ 3.42 E-02 →	- 1.466	5.613 E+00 →	0.749	6.09 E-03 →	- 2.215
p-nitro-toluene[R] (pnT)	2.11 E-4 →	- 3.677	1.231 E+00 →	0.090	1.71 E-04 →	- 3.767
2,4-dinitro-toluene[R](DNT)	2.86 E-07 →	- 6.544	1.537 E+00 →	0.187	1.86 E-07 →	- 6.731
Pesticides[SM]:						
DDT	~1.316 E-10 →	- 9.881	3.39 E-06 →	-5.470	3.89 E-05 →	- 4.41
Dieldrin (diel)	~1.316 E-10 →	- 9.881	6.56 E-04 →	-3.183	2.01 E-07 →	- 6.70
Solvents:						
Water[SM] (wat)	3.126 E-02 →	- 1.505	5.556 E+04 →	4.745	5.63 E-07 →	- 6.250
TCE[V]	≥ 1.026 E-01 →	- 0.989	8.365 E+00 →	0.923	1.23 E-02 →	- 1.911
Other Solids:						
Naphthalene[SM]	3.026E-4(25C) → 1 torr (53°C)	-3.519	2.578E-01 →	-0.589	1.117E-03 →	-2.930
Ice	6.025 E-03 → 4.579 torr (0°C)	-2.220	5.556E+04 →	4.745	1.084E-07 →	-6.96

[1] C_S versus P_v is plotted in Figure 6.4 using the compound abbreviations as plotting symbols.
[2] Superscripts indicate reference: V = Verschueren (1983), SM = Stumm and Morgan (1981), R = Rosenblatt et al. (1989).
[3] Superscript R also indicates that P_v's were estimated using Clausius-Clapeyron equation (Rosenblatt et al., 1989). TNT value is interpolated. Supercooled vapor pressures or modified for solid condition; k_H is estimated as $(P_v(torr) \times MW$ (g $\cdot$ mol^{-1}))/ (Solubility (g $\cdot$ m^{-3}) $\times$ 760 (torr/atm)). (1 atm = 760 torr = 760 mm Hg at 0°C = 1.01325 $\times$ 10^5 Pa = 1.01325 bars.)

$$\frac{d \ln P_v}{d T} = \frac{\Delta H_v}{\Delta Z R T^2} \qquad (6\text{-}2)$$

The compressibility factor, ΔZ, may be calculated as follows (Grain 1990):

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$$\Delta Z = \frac{P_v \, \Delta V_{VL}}{R \, T} \tag{6-3}$$

where ΔV_{VL} is the volume difference between vapor and condensed (liquid or solid) condition [L^3] and R is in $cm^3 \cdot atm \cdot K^{-1}$ (here only; usually expressed in $cal \cdot mol^{-1} \cdot K^{-1}$). Since V_V is usually several orders of magnitude greater than $V_{S(or\,L)}$, $\Delta V_{VL} \approx V_V$, and $\Delta Z \approx 1$ for an ideal gas.

A common integral form of Equation 6-2 is used to estimate vapor pressures of low volatility compounds at environmental temperatures based on observations at higher temperatures (Grain 1990):

$$\log P_v = A - \frac{B}{T_K} \tag{6-4}$$

where A and B are empirical coefficients, and T_K is Kelvin temperature. Rosenblatt et al. (1989) present a table of these coefficients for common XACs (for P_V in torr), a portion of which is presented below (Table 6.2).

Table 6.2 Clausius-Clapeyron Equation Parameters for Estimating Vapor Pressures for Several Explosives[1]			
XAC	A	B	Reference
TNT	14.53 12.31 ± 0.34	5,900 5,175 ± 105	Cundall et al. (1981) Pella (1977)
2,4-DNT	13.08 ± 0.19	4,992 ± 59	Pella (1977)
2,6-DNT	13.99 ± 0.18	5,139 ± 52	Pella (1977)
DNB	8.56	3,170	Macksimov (1963)
TNB	13.29	5,608	Cundall et al. (1981)
RDX	15.12 11.87	7,011 5,850	Cundall et al. (1981)
HMX	14.72	8,407	Cundall et al. (1981)
Tetryl	15.19	6,987	Cundall et al. (1981)
[1] From Rosenblatt et al. (1989).			

Most explosives and many of the associated contaminants are crystalline solids at environmental temperatures (0° to 30°C). Vapor pressures for solid explosives are very low, typically on the order of 10^{-4} to 10^{-11} torr ($10^{-2} - 10^{-9}$ Pa; $10^{-7} - 10^{-14}$ atm) at 25°C. This range of P_v is low relative to many common, liquid, volatile organic contaminants (VOCs), which range typically

between 10^{-5} and 300 torr (Grain 1990). The P_v's for explosives are of the same order of magnitude as pesticides; though pesticides tend to have lower aqueous solubilities; lower water solubility tends to enhance partitioning out of aqueous solutions. Unfortunately, experimental data on XAC sublimation are sparse. Though not typically considered a major pathway for explosives dispersal in the environment, the possibility should not be dismissed without justification, particularly with respect to lower molecular weight co-contaminants. Soil temperatures conceivably could be elevated by solar insolation or brush fires. The subject of sublimation merits further investigation but is not a high priority in light of still greater uncertainties regarding other processes.

6.2 Volatilization of Solutes

Henry's Law describes the equilibrium partitioning of an ideal constituent between the vapor and aqueous phases. Air phase concentration of constituent x ($C_{x(A)}$) is a constant proportion of the aqueous phase concentration ($C_{x(W)}$, mole fraction) at Kelvin temperature T (Stumm and Morgan 1981):

$$K_H \equiv \frac{C^o_{S\,x(A)}}{C^o_{S\,x(W)}} = \frac{P^o_{Vx}}{C^o_{S\,x(W)}\,R\,T}$$

$$= \frac{C_{x(A)}}{C_{x(W)}} = \frac{P_{Vx}}{C_{x(W)}\,R\,T} = \frac{k_H}{R\,T} \tag{6-5}$$

where K_H and k_H are, respectively, the dimensionless and dimensioned [pressure$\cdot$L^{3}mol^{-1}] forms of the Henry's law constants. $C^o_{Sx(A)}$ and $C^o_{Sx(W)}$ are the saturated (subscript S) concentrations of compound x in the air and water phases (subscripts A or W, respectively) at equilibrium with pure compound (indicated by superscript "o"). P^o_{Vx} is the vapor pressures (P) in equilibrium with pure compound; P_{Vx} is the partial pressure of x in the gas phase. $C_{x(A)}$ and $C_{x(W)}$ are the unsaturated, equilibrium concentrations [M$\cdot$L^{-3}] of x in the air and water phases, respectively. As indicated by Equation 6.5 the two Henry's constants are related: $K_H = k_H / (RT)$. Partial pressure of x (P_{Vx}) may be estimated by:

$$P_{Vx} = \frac{C_{x(W)}\,P^o_{Vx}}{C^o_{S\,x(L)}} \tag{6-6}$$

Note that the k_H Henry's constant is approximated by the ratio of vapor pressure to solubility:

$$k_H \simeq \frac{P^o_{Vx}}{C^o_{S\,x(W)}}$$

(6-7)

This relation is plotted in Figure 6.4 for several explosives and associated solutes (data in Table 6.1).

The volatilization of a solute involves at least three subprocesses: (1) advective and/or diffusive transport to an air interface, (2) mass transfer across the interface, and (3) vapor transport away from the interface. Any one of these processes can be rate limiting, but the interface mass transfer is probably the limiting phenomena in XAC volatilization.

Dual resistance model. Several conceptual models have been proposed to describe volatilization of solutes from surface water (i.e., not in porous media), but the dual resistance model has been the most widely used. The two-film, mass transfer model (Liss and Slater 1974, Mackay and Leinonen 1975) envisages the mass flux across an air-water interface as being controlled by molecular diffusion through two, infinitesimally thin layers at the interface—a vapor film and an aqueous film (see Figure 6.3). Mass transfer is limited by the more resistant of these two films. Air-water partitioning is assumed to be described by Henry's law. Bulk water and vapor phases are assumed to be well mixed; lack of mixing in either phase (e.g., a stratified water column), would cause overestimates of volatilization.
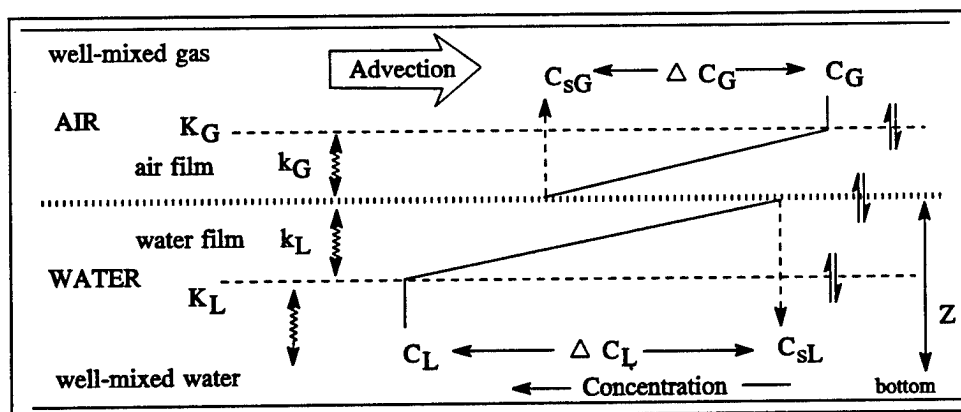
Figure 6.3. Dual resistance model of Liss and Slater (1974) for mass flux across the air-water interface

The steady-state mass flux, J [$M \cdot L^{-2} \cdot T^{-1}$], across this system is equal to the fluxes across each of the films as described by Thomas (1990a):

$$J = k_L \left(C_{SL} - C_L \right) = k_G \left(C_G - C_{sG} \right)$$

(6-8)

where k_L and k_G are exchange coefficients [L·T^{-1}] across the liquid and gas films, respectively, C_L and C_{sL} are bulk and interface liquid phase concentrations [M·L^{-3}], and C_G and C_{sG} are bulk and interface gas concentrations [M·L^{-3}]. Assuming C_{sG} is at equilibrium with the liquid and a dimensionless Henry's constant ($K_H = C_{sG} / C_{sL}$), then Equation 6-8, becomes (Thomas 1990a):

$$J = \frac{C_G - K_H C_L}{\left[\dfrac{1}{k_G} + \dfrac{K_H}{k_L}\right]} = \frac{\dfrac{C_G}{K_H} - C_L}{\left[\dfrac{1}{K_L} + \dfrac{1}{K_H k_G}\right]} \qquad (6\text{-}9)$$

Defining the net mass transfer coefficients for the gas (K_G) and liquid (K_L) phase films as:

$$\frac{1}{K_G} = \left[\frac{1}{k_G} + \frac{K_H}{k_L}\right] \quad \text{and}$$

$$\frac{1}{K_L} = \left[\frac{1}{k_L} + \frac{1}{K_H k_G}\right] \qquad (6\text{-}10)$$

and substituting into Equation 6-9 yields:

$$J = K_G \left(C_G - K_H C_L\right) = K_L \left[\frac{C_G}{K_H} - C_L\right] \qquad (6\text{-}11)$$

or in dimensioned form:

$$J = K_G \left[C_G - \frac{k_H C_L}{R\,T}\right] = K_L \left[\frac{C_G}{k_H /(R\,T)} - C_L\right] \qquad (6\text{-}12)$$

Of course, the dual resistance model would be invalid for porous media without significant reworking. Thorough mixing would be rare in any porous medium. The air-water interface is highly irregular in porous media. Yet certain of the concepts may be useful in porous media applications.

The value of the Henry's constant (k_H) provides a qualitative insight into the volatility of a solute. Thomas (1990a) reports some general behavioral trends (citing D. Mackay; also see Table 6.1 and Figure 6.4):

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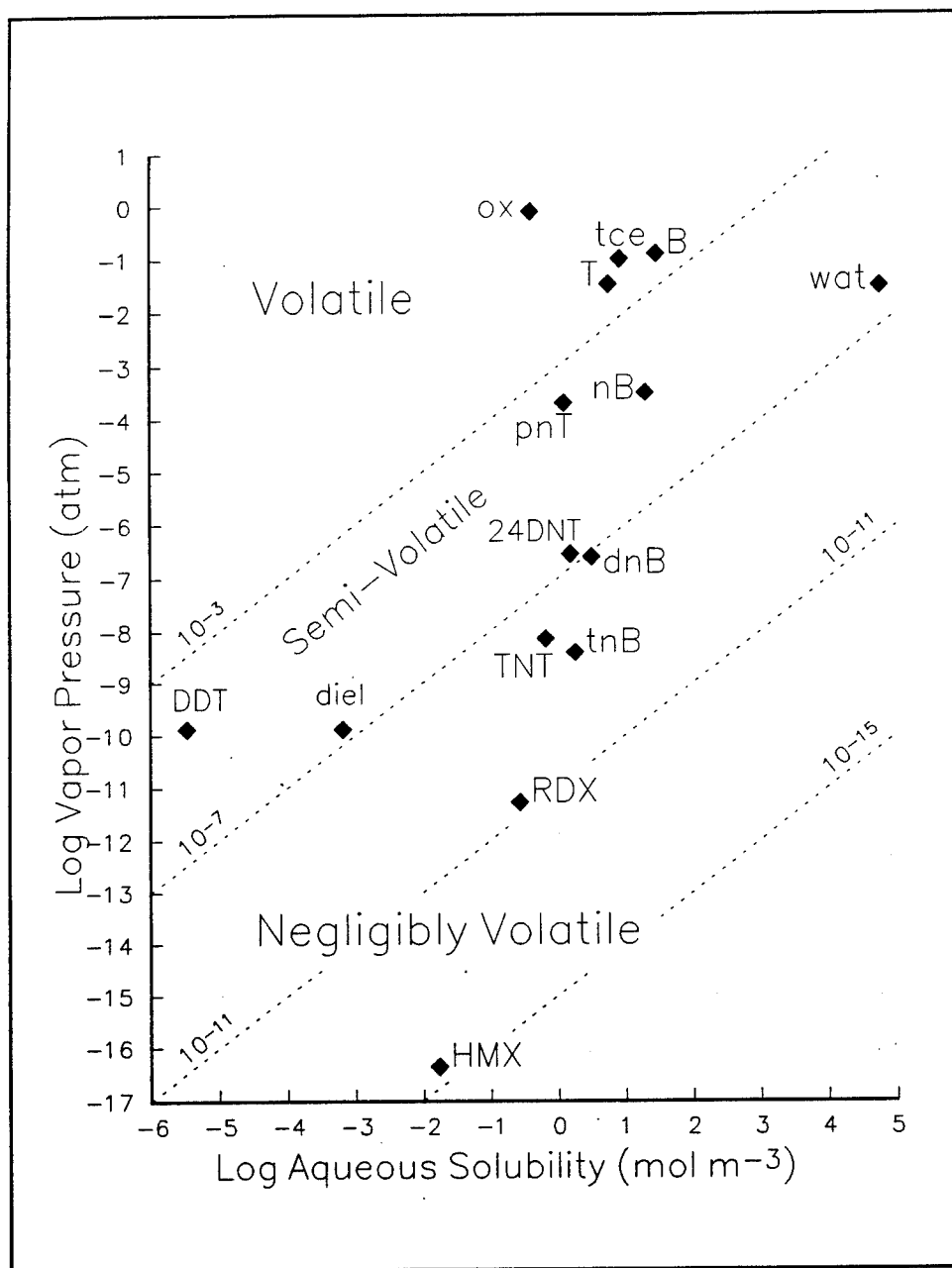
Figure 6.4. The log of vapor pressure (atmospheres) versus log of aqueous
solubility (moles per cubic meter) for representative XACs and,
for comparison, several pesticides and organic solvents (25°C;
see Table 6.1 for abbreviations and values). Henry's law con-
stants ($k_H \approx P_v/C_{sol}$) are defined by the sloping, dotted lines
which also delineate regions of volatile organics (k_H above
10^{-3} atm·m^3·mol^{-1}), essentially nonvolatile organics (k_H below
10^{-7} atm·m^3·mol^{-1}), and semivolatile organics with k_H between
10^{-7} and 10^{-3} atm·m^3·mol^{-1} (Thomas 1990a)

- $k_H < 10^{-7}$ atm·m^{-3}·mol^{-1}: essentially nonvolatile; less volatile than water (3×10^{-7}).

- $10^{-7} \leq k_H \leq 10^{-5}$ atm·m^{-3}·mol^{-1}: slow volatilization, dependent on K_h. Gas phase resistance dominates liquid phase resistance by a factor of 10 or more. Rate limited by slow molecular diffusion through air.

- $k_H \leq 2\times10^{-5}$ atm·m^{-3}·mol^{-1}: tendency to partition into the liquid phase, therefore slow volatilization, dependent on k_H. Gas phase resistance dominates.

- $10^{-5} \leq k_H \leq 10^{-3}$ atm·m^{-3}·mol^{-1}: both liquid and vapor film resistances significantly influence volatilization rates.

- $k_H > 10^{-3}$ atm·m^{-3}·mol^{-1}: volatile; water film resistance dominates mass transfer by a factor of 10.

For highly volatile compounds ($k_H > 10^{-3}$), $k_L \gg k_H k_G /(RT)$, with a negligible atmospheric concentration (C_G), the transfer is independent of k_H and $J = k_L C$, i.e., a pseudo first-order process.

The very low Henry's constants of XACs indicate that volatilization is limited by water film resistance; thus, volatilization descriptors for XACs may neglect air film resistance. Molecular oxygen exchange is controlled by the air film resistance. Many compounds are surface active (i.e., surfactants) which tend to accumulate at the air-water interface. Most interface resistance models do not capture explicitly the phenomena of solute accumulation in the interfacial microlayer or its effects on the mass transfer of other solutes.

6.3 Vapor Transport in Soils and Porous Media

The volatilization descriptors for open water systems (Section 6.2) are useful only for conceptualization of the microscale, interfacial phenomena in porous media. Volatilization from soil waters is much more complicated than from surface waters because of the increased influence of adsorption to soil solids, the increased diffusion path lengths and tortuosities, the general lack of well-mixed conditions in either the water or air phases, and the extreme irregularity possible in the soil water-air interface.

No truly predictive volatilization models are available for soils. Considerable research has been conducted to evaluate pesticide losses from agricultural soils and the subsurface transport of volatile organic compounds (VOCs), e.g., benzene, toluene. A rigorous model to describe the volatilization of XACs from soils and groundwater plumes would need to consider the following (Thomas 1990b):

a. *Contaminant chemistry.* Aqueous solubility, molecular structure (functional groups), air-water-soil partitioning behavior in complex multicomponent systems, and the phase(s) and distribution (e.g., crystalline solid dispersed in soil horizon) control fate and transport.

b. *Soil or aquifer properties.* Media composition (e.g., oxyhydroxides, organic carbon content, mineralogy), structure (e.g., porosity, macroporosity, permeability), and ground cover are primary controls on advective transport.

c. *Environmental variables.* Specifically temperature, precipitation, infiltration, water saturation and relative humidity, atmospheric conditions (e.g., wind, air pressure), and Eh-pH conditions all can influence transport processes.

Subsurface, vapor phase solutes are subject to the same processes affecting aqueous solutes—advection, dispersion, diffusion, sorption, and other reactions—as well as saturation-dependent permeability (see Section 3.4). Two approaches to describing vapor phase transport in porous media are with an advective-dispersion equation similar to that for unsaturated water flow or using bulk mass transfer models. Descriptors for vapor phase advection-dispersion transport (ADT) can be relatively sophisticated, requiring numerous empirical parameters describing multiphase flow, interphase mass transfer, etc. Descriptors for volatilization loss from soils are largely empirical and semiquantitative; yet, they are useful for first-order estimates in risk analysis of hazardous waste sites.

Volatilization from a solute plume obviously requires direct air contact. Within the vadose zone the extent of this contact is a function of saturation. As the plume enters the phreatic (saturated) zone, the plume-air contact area is approximately the lateral extent of the plume. As any neutrally buoyant (or more dense), solute plume migrates down gradient, it also tends to migrate downward, away from the water table due to vertical recharge from precipitation. This phenomenon obviously precludes further volatilization in the distal plume.

Soil water content may significantly influence volatilization, particularly at low saturation levels (S_w on the order of a few percent). In dry soils organics may adsorb strongly to solids. With the introduction of water, the polar water molecules compete for sorption sites and surfaces, and if the previous adsorbate is less polar, it tends to be displaced into either aqueous or vapor solution, thereby increasing its partial pressure. At water saturations beyond that required to form a monolayer, the effect of increased wetting decreases. As the partitioning coefficient increases, the effect of S_w on volatilization decreases (Thomas 1990b, Valsaraj and Thibodeaux 1992).

Vapor phase advective-diffusive transport

Vapor constituent dispersal is controlled primarily by advection in response to pressure gradients which may arise from vapor density variation or from meteorological or engineered pressure variations (e.g., bioventing, vapor extraction). Vapor density is a function of the contaminant volatility and composition but is strongly influenced by the porous medium composition and environmental conditions, particular humidity.

The flow equation for the vapor phase is analogous to the unsaturated water flow equation. Vapor phase seepage velocity (v_V) is:

$$v_V = - \frac{k_{rV} \, k_i \, \rho_V g}{\mu_V n_e} \left[\nabla \frac{P_V}{\rho_V g} + \nabla z \right] \tag{6-13}$$

where the saturation (or pressure) dependence of flow is described by the relative permeability to the vapor phase, k_{rV}, and ∇ indicates a spatial gradient. The relative permeability for the vapor phase ($0 \leq k_{rV} \leq 1$; dimensionless) is nonlinearly dependent on capillary pressure (P_c) and/or phase saturation (S_α), and serves to describe the reduction in effective permeability caused by the interference by any nonvapor phase(s). The intrinsic permeability, k_i [L^2], is a property of the medium only. Since the vapor phase is typically the nonwetting phase in soil and aquifer materials, air tends to occupy the larger pores. Relative to aqueous phase transport of XACs, the lower viscosity of the vapor phase (μ_V) reduces resistance to advection; conversely, the low vapor phase concentrations, density, and pressure gradients tend to reduce the effectiveness of vapor transport. A one-dimensional transport equation for vapor transport is

$$\frac{\partial C_V}{\partial t} = D_V \frac{\partial^2 C_V}{\partial z^2} + v_V \frac{\partial C_V}{\partial z} \tag{6-14}$$

where C_V is the vapor phase concentration, and D_V is an effective dispersion coefficient.

Volatilization of constituents that are heavier than air molecules (e.g., halogenated aromatics) increase the bulk vapor density (ρ_v), which if sufficient may induce flow down the pressure gradient ($\rho_v g$ in Equation 6-13). The XAC vapors are probably too dilute in the vapor phase to affect bulk vapor density appreciably or flow due to density (pressure) gradients.

Diffusive transport. Vapor transport in porous media is impeded, relative to that in free air, because of the increased length and tortuosity (τ_{sa}) of the flow path. Several definitions for tortuosity have been proposed. The ratio of

air-filled porosity (n_{sA}) to total porosity (n_T) is one definition of a tortuosity factor for soil air (τ_{sa}) (Millington and Quirk 1961):

$$\tau_{sA} = \frac{n_{sA}^{10/3}}{n_T^2} \qquad (6\text{-}15)$$

where the porosities may be determined experimentally. Millington (1959) suggests an exponent of only 7/3 for porous media (Johnson and Perrott 1991). Primary controls on tortuosity and permeability include soil structure (e.g., pore interconnectivity) and water saturation. Tortuosity tends to increase with air saturation (more small channels open to air flow); reduced water saturation also tends to increase the amount of interface area available for volatilization.

The apparent soil air (or vapor) diffusion coefficient, D_{sA}, is affected by water saturation (Thomas 1990b):

$$D_{sA} = \tau_{sA} \frac{D_A}{\rho_{bA}} \frac{d\,\rho_{sA}}{d\,C_{sA}} \qquad (6\text{-}16)$$

where D_A is the molecular diffusion coefficient in air [$L^2 \cdot T^{-1}$], ρ_{bA} and ρ_{sA} are, respectively, the densities [$M \cdot L^{-3}$] of bulk air and soil air, and C_{sA} is the compound concentration in the soil air. Equation 6-16 indicates that vapor diffusion increases with air-filled porosity increases (lower τ_{sA}). Vapor density increases with vapor concentration (ρ_{sA} / C_{sA}) up to a critical concentration, beyond which aqueous diffusion begins to dominate diffusive transport. Neglecting the bulk and vapor density effects, Equation 6-16 becomes simply (Thomas 1990b):

$$D_{sA} = \tau_{sA} D_A \qquad (6\text{-}17)$$

An effective diffusion coefficient (D_e) may be defined as the combined influence of solute diffusion in the aqueous phase, described by D_W, and diffusion within the soil air (D_A). Ehlers et al. (1969) showed that vapor pressure and vapor diffusion are affected by atmospheric pressure, whereas liquid phase diffusion is not affected:

$$D_e = D_W + D_A \left[\frac{P_o}{P}\right] \qquad (6\text{-}18)$$

where P and P_o are the ambient and reference (standard atmosphere) pressures. Typically, (P_o/P) is close to 1 for natural pressure variations but may be significantly smaller under vacuum extraction conditions (low P). Molecular diffusion coefficients for vapor transport are typically 10^4 times greater than in the water phase (see Table 3.2).

Capillarity effects. Effect of the negative capillary pressure encountered above the water table presents another interesting complication to volatilization modeling in porous media. Water and any solutes can be drawn upward from the water table by capillary action (capillary fringe); water in the vadose zone may be spread by capillarity as well. With sufficient evaporation of the more volatile water solvent, XAC concentrations could increase, perhaps to a point at which precipitation of solids is possible. This wick phenomenon may affect XAC transport, though its significance is not substantiated by field observations.

Soil flux models

Many semiempirical models have been proposed to describe the mass flux from contaminated soils and/or the concentration profiles within the soil. Most of these models either describe mass flux without regard to partitioning or assume equilibrium air-water partitioning, which is likely to be violated under conditions of higher soil water content, flowing water, and for sparingly volatile solutes. A few representative descriptors are presented here in order to identify some of the common significant parameters in modeling the phenomenon.

A general expression for vertical, diffusive flux, J [$M \cdot L^{-2} \cdot T^{-1}$], is:

$$J = - n_{sA} D_{sA} \frac{\partial C_{sA}}{\partial z} \tag{6-19}$$

with z positive in the downward direction (Charbeneau and Daniel 1992, Jury and Ghodrati 1989). Substituting Equation 6-17 into Equation 6-19 yields:

$$J = - \tau_{sA} n_{sA} D_A \frac{\partial C_{sA}}{\partial z} \tag{6-20}$$

Thomas (1990b) reviews several models for estimating mass flux and/or concentration profiles for volatile compounds in soils. Several methods may be applicable to the volatilization of sparingly volatile compounds such as XACs. Soils contaminated by XACs may include burn pits, leach fields, or lagoon sediments.

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Hartley model. Hartley (1969) proposed a simple model based on heat balance to estimate volatilization of low volatility compounds. The flux J [$M \cdot L^{-2} \cdot T^{-1}$] at the soil-air interface is

$$J = \frac{D_v \, \rho_{\max} \left(1 - h\right)}{\delta}$$ (6-21)

where ρ_{max} is the saturated vapor concentration [$M \cdot L^{-3}$], h is atmospheric humidity ($0 \leq h \leq 1$), and δ is the thickness [L] of the stagnant air through which compounds must diffuse.

Hamaker method. Hamaker (1972) developed a pair of expressions for volatilization loss Q_t [$M \cdot L^{-2}$] from a contaminated soil of semi-infinite length (i.e., thick relative to the zone from which contaminant is depleted). At time t [T], the cumulative loss is:

$$Q_t = 2 \, C_o \sqrt{\frac{D_{sA} \, t}{\pi}}$$ (6-22)

where C_o is the initial concentration in the soil [$M \cdot L^{-3}$]. A second expression includes accounts for aqueous phase transport as well. For a volatile solute:

$$Q_t = \frac{P_V}{P_{H_2O}} \frac{D_A}{D_{H_2O}} \, (f_w)_V + C_w \, (f_w)_L$$ (6-23)

where f_w is the areal water loss [$M \cdot L^{-2}$] and the subscripts V and L relate to volatilization and water loss (e.g., drainage), respectively. If a compound has a vapor pressure (P_v) and diffusion coefficient in air (D_a) less than that of water, volatilization loss from solution is reduced. Of course, this expression requires an estimate of soil water flux as well as aqueous concentrations (C_w, $M_{solute} \cdot M_{solvent}^{-1}$).

Jury et al. models. Jury et al. (1980) developed a flux estimation model with or without wick effects. Total concentration of the solute (C_T) is described simply as:

$$C_T = \rho_b \, S + \theta_W \, C_W + \theta_A \, C_A$$ (6-24)

where S, C_W, and C_A are the sorbate [$M \cdot M^{-1}$], solute [$M \cdot L^{-3}$], and vapor concentrations [$M \cdot L^{-3}$], respectively, ρ_b is the bulk density [$M \cdot L^{-3}$], θ_w is the

volumetric water content $[L^3 \cdot L^{-3}]$, and θ_a is the volumetric air content $[L^3 \cdot L^{-3}]$. The total mass flux J_T $[M \cdot L^{-2} \cdot T^{-1}]$ is described by:

$$J_T = -D_{sA} \frac{\partial C_A}{\partial z} - D_W \frac{\partial C_W}{\partial z} - q_W C_W \qquad (6\text{-}25)$$

which includes diffusion in the soil air (D_{sA}) and water (D_w) phases as well as water flux q_w $[L^3 \cdot L^{-2} \cdot T^{-1}]$ or specific discharge through the soil.

Equations 6-24 and 6-25 may be solved with the continuity equation ($\partial C_T/\partial t + \partial J/\partial z = 0$) to calculate soil column concentrations, flux, and mass lost (Thomas 1990b). The model entails the following assumptions:

a. Henry's law describes the partitioning between soil water and soil air phases.

b. A linear adsorption isotherm— $S = \alpha C_W + \beta$, where α and β are isotherm parameters—describes partitioning between water and solid phases over the concentration range of interest.

c. Constant diffusion coefficients in a homogeneous soil.

d. Water flux q_W is negligible or equal to the evaporation rate.

e. Atmospheric gas concentrations are negligible.

f. The medium is infinitely long or deep.

Substituting equilibrium partitioning expressions into Equations 6-24 and 6-25 and expressing concentrations in terms of the air phase concentration yields:

$$C_T = \epsilon C_{sA} + \gamma \qquad (6\text{-}26)$$

where ϵ and γ are derived parameters:

$$\epsilon = \rho_b K_H \alpha + \theta_w K_H + \theta_a \qquad (a)$$
$$\gamma = \beta \rho_b \qquad (b) \qquad\qquad (6\text{-}27)$$

and

$$J_T = -D_e \frac{\partial C_{sA}}{\partial z} - V_e C_{sA} \tag{6-28}$$

where an effective diffusion coefficient (D_e) and effective aqueous phase velocity (V_e) are defined as:

$$
\begin{aligned}
D_e &= D_{sA} + K_H D_W & (a)\\
V_e &= K_H q_W & (b)
\end{aligned}
\tag{6-29}
$$

Likewise, the continuity equation, expressed in terms of the gas phase concentration, becomes:

$$\epsilon \frac{\partial C_{sA}}{\partial t} = D_e \frac{\partial^2 C_{sA}}{\partial z^2} + V_e \frac{\partial C_{sA}}{\partial z} \tag{6-30}$$

For no water flux ($q_w = 0$) and the following boundary conditions:

$$
\begin{array}{llll}
C_{sA} = 0 & at \quad z = 0, \quad t \geq 0 & (a)\\
C_{sA} = (C_{t_0} - \gamma)/\epsilon & at \quad t = 0, \quad z \geq 0 & (b) & (6\text{-}31)\\
C_{sA} = (C_{t_0} - \gamma)/\epsilon & at \quad t = 0, \quad z \geq \infty & (c)
\end{array}
$$

The mass flux at the air-soil interface, J(0,t), and concentration profile $C_{sa}(z,t)$ descriptors are:

$$J_T(0, t) = -(C_{T0} - \gamma) \sqrt{\frac{D_e}{\epsilon \pi t}} \qquad (a)$$

and

$$C_g(z, t) = \frac{C_{T0} - \gamma}{\epsilon} \, erf\left[\frac{z}{2}\sqrt{\frac{D_e t}{\epsilon}}\right] \qquad (b)$$

$$\tag{6-32}$$

where C_{T0} is the total initial concentration in the soil $[M \cdot L_{soil}^{-3}]$. For $q_w = 0$, the total loss by volatilization is found by integrating the flux equation (Equation 6-32a):

$$Q_t(t) = 2(c_{t,0} - \gamma) \sqrt{\frac{D_e t}{\pi \epsilon}}$$ (6-33)

If water flux through the soil is significant ($q_w > 0$), the flux expression is

$$J(0, t) = -(c_{t,0} - \gamma) \sqrt{\frac{D_e}{\epsilon \pi t}} \, e^{-w^2}$$

$$-V_e \left[\frac{c_{t,o} - \gamma}{2\epsilon} \right] [1 + erf(w)]$$ (6-34)

where

$$w^2 = \frac{V_e^2 t}{4 D_e}$$

and the concentration profile at time t is described by:

$$c_g(z, t) = \left[\frac{c_{t0} - \gamma}{\epsilon} \right]$$

$$\left[1 - \frac{1}{2} erfc \left[\frac{z + \frac{V_e t}{\epsilon}}{2\sqrt{\frac{D_e t}{\epsilon}}} \right] - \frac{1}{2} e^{-\frac{V_e z}{D_e}} erfc \left[\frac{z - \frac{V_e t}{\epsilon}}{2\sqrt{\frac{D_e t}{\epsilon}}} \right] \right]$$ (6-35)

where the complementary error function, $erfc(x)$ is $(1 - erf(x))$.

Mayer et al. models. Mayer, Letey, and Farmer (1974) developed a set of five solutions for the diffusion equation for a variety of boundary conditions (see Table 6.3). Only diffusive transport is modeled; thus estimates by these models tend to underestimate volatilization losses (Thomas 1990b). All solutions assume a uniform initial concentration C_o over the contaminated length L. Models I, II, and III assume that atmosphere movement is sufficient to maintain a zero concentration at the air-soil interface; model IV permits a nonzero concentration. Model V includes an immobile air zone between the soil-air interface and free, mobile air; this zone may be conceptualized as a vegetated horizon, for example. For sparingly volatile compounds such as XACs, a surface air concentration of zero is a reasonable approximation;

Table 6.3
Summary of the Five Models of Mayer et al. (1974) for Volatilization From Soil

Model	Concentration at Soil-Air Interface	Lower Boundary	Comments
I	0	No flux	Uniform C_o over length L
II	0	No flux	—
III[1]	0	Diffusive flux	—
IV	C_a	No flux	—
V[1]	0 at mobile air interface C_a at immobile air-soil interface	No flux	Immobile air zone above soil-air contact
[1] Models III and V are discussed in text.			

downward flux would be likely so the no flow, lower boundary would not be realistic. Only models III and V are reviewed here.

Model III assumes a zero concentration at the air-soil interface but allows diffusive loss at the base of the column. The mass efflux, $J(0,t)$, descriptor is

$$J(0,t) = \frac{D_{sa} C_o}{\sqrt{\pi D_{sa} t}} \left[1 - e^{\frac{-L^2}{4 D_{sa} t}} \right]$$
(6-36)

For small values (<0.01) of the exponential term, $exp(-L^2/(4D_{sa} t))$, the term in parentheses in Equation 6-36 reduces to 1, introducing less than a 1 percent error (equivalent to $t < L^2/(18.4 D_{sa})$. The concentration profile, $C(z,t)$, may be expressed as:

$$C(z,t) = -\frac{C_o}{2} \left[2 \, erf \left[\frac{z}{2 \sqrt{D_{sa} t}} \right] \right.$$
$$\left. - erf \left[\frac{z-L}{2 \sqrt{D_{sa} t}} \right] - erf \left[\frac{z+L}{2 \sqrt{D_{sa} t}} \right] \right]$$
(6-37)

Model V introduces a stagnant air layer of thickness d at the base of the air column through which vapors must diffuse after escaping the soil. This layer may be conceptualized as a vegetated zone in which atmospheric air flow is impeded. The mass efflux, $J(0,t)$, descriptor is:

$$J(0,t) = 2 D_{sa} C_o \sum_{n=1}^{\infty} \left[\frac{e^{-D \alpha_n^2 t} \left[\dfrac{D_v R_o}{D_{sa} d} \right]^2}{L \left[\dfrac{D_v R_o}{D_{sa} d} \right]^2 + L \alpha_n^2 + \left[\dfrac{D_v R_o}{D_{sa} d} \right]} \right] \qquad (6\text{-}38)$$

where D_v is the diffusion coefficient in air [$L^2 \cdot T^{-1}$], and R_o is an isotherm coefficient, defined as the ratio of air concentration to soil concentration, which may be approximated by the Henry's constant (K_H) to the linear sorption coefficient (K_d). The α_n terms are the positive roots of:

$$\alpha_n \tan(\alpha_n L) = \frac{D_v R_o}{D_{sa} d} \qquad (6\text{-}39)$$

where n is the number of terms in the summation, which is truncated after convergence to 2 or 3 significant figures, typically between 2 and 10 (Thomas 1990b). The concentration profile, $C(z,t)$, is described as:

$$C(z,t) = \frac{2 D_v R_o C_o}{D_{sa} d} \sum_{n=1}^{\infty}$$

$$\left\{ \frac{e^{-D \alpha_n^2 t} \cos[\alpha_n (L - z)]}{L \cos(\alpha_n) \left[L \left[\dfrac{D_v R_o}{D_{sa} d} \right]^2 + L \alpha_n^2 + \left[\dfrac{D_v R_o}{D_{sa} d} \right] \right]} \right\} \qquad (6\text{-}40)$$

Perhaps this model could be adapted to estimate volatilization from a contaminant plume by redefining the stagnant air zone as the vadose zone. The diffusion coefficients for the stagnant air and soil air would be substituted with, respectively, the soil air and soil water diffusion coefficients. The contaminant zone dimension would become the plume thickness.

Thomas (1990b) recommends two methods for estimating volatilization in cases where advective water flow—either down as infiltration or upward as capillary rise—is an influencing factor: 1) the relatively complex model of Jury et al. (1980), and 2) the relatively simple Hamaker (1972) method.

6.4 Vapor Transport of Explosives and XACs

Sublimation and volatilization of explosives appear to be negligible relative to other transport mechanisms in soils and in the subsurface. Volatilization may be neglected for most short-term research or remediation investigations. However, volatilization may become worthy of consideration in long-term assessments of XAC-contaminated soils. Explosives in soils may be subject to significant heating by solar insolation (and perhaps brush fires) which could enhance volatile losses from soils. The vapor pressures for XACs in soils will likely be controlled by equilibrium with crystalline (or noncrystalline) compounds when such are present.

Vapor phase transport may be relevant in assessing the fate of semivolatile or volatile compounds associated with explosives contamination (e.g., nitrobenzene, ammonia), or non-XAC constituents that may affect natural or engineered biotransformations (e.g., oxygen, methane). Ideally, field-scale monitoring of a XACs-contaminated aquifer would include measurements of key volatile reactants or reaction products, such as O_2, N_2, or NH_3, as indicators of active reaction mechanisms.

7 Biotransformation

Subsurface microorganisms—predominantly bacteria and fungi—are capable of mediating a variety of transformation reactions involving explosives and explosives associated compounds (XACs). Complete degradation (mineralization) of synthetic organic compounds (xenobiotics) to innocuous gases (e.g., CO_2, N_2), water, and inorganic salts (e.g., Cl^-, NO_3^-) is the ultimate goal in bioremediation.

Bioremediation is certainly the most tantalizing remediation technology for explosives and other organic contaminants because of the possibility that mineralization can be achieved. The potential cost savings are significant relative to chemical or physical treatment processes. Unfortunately, many xenobiotics are recalcitrant, that is, they are resistant to attack by microbial enzymes. Thus, even under ideal conditions such as in a bioreactor (e.g., composting), biotransformations may be incomplete. Under field conditions, mineralization often is not realized because of the difficulties in delivering required nutrients, and perhaps microbes, to the contaminated zone. A major hindrance to the general application of in situ bioremediation in complex hydrogeochemical, field environments is our incomplete understanding of the interacting processes in these environments and our limited ability to overcome impediments imposed by these complexities.

Appropriate conceptual, mathematical, and numerical modeling of microbial processes is critical to the development and evaluation of our evolving understanding. The conceptualization requires consideration of microbial ecology, biochemistry, and coupling to multiple abiotic processes. This review of biotransformation begins with a brief discussion of microbial ecology and energetics (Section 7.1). Several approaches to describing microbial growth and metabolism kinetics are discussed (Sections 7.2 and 7.3). Coupling of biotic with abiotic processes is reviewed (Sections 7.4, 7.5, and 7.6).

The general term microorganism used herein refers to any member of a typically diverse community of micron-scale, interacting organisms, including viruses, bacteria, fungi, etc., and their protozoan and invertebrate predators or grazers. This diversity of microorganisms always must be considered when transferring to field application any conceptual or mathematical models developed under controlled laboratory conditions with special strains of

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microorganisms. The term consortium is reserved for reference to a subset of the microorganism population responsible for a particular reaction or set of reactions. The term implies that a symbiotic relationship exists between members of the consortium resulting in a degradation of the target compound that would not proceed (or at a lesser rate) in the absence of a consortium member(s).

7.1 Subsurface Microbial Ecology

Distribution and size

Microorganisms have been recovered from virtually all subsurface environments that may affect groundwater resources—soils, shallow and deep aquifers, arid and cold regions, and petroleum reservoirs (Ghiorse and Wilson 1988, Fredrickson and Hicks 1987). Microbial population density, viability, and, most importantly for remediation purposes, ability to degrade contaminants vary dramatically. Bacteria are the predominant microorganism in shallow aquifers, though other organisms are present, such as eucaryotes and fungi (Fredrickson and Hicks 1987). Ghiorse and Wilson (1988) review early (1980-1987) efforts to characterize the microbial ecosystems of shallow aquifer systems.

Soil bacterial populations are typically high, ranging between 10^5 and 10^8 cells per gram of soil, with the majority being viable (metabolically active). Population densities tend to drop off with depth in the soil and below the soil horizons. In pristine aquifers numbers range between 10^5 and 10^7 cells per gram of sediment and their viability varies tremendously from zero to nearly 100 percent (Ghiorse and Wilson 1988). Enumeration data on indigenous bacteria in aquifer systems are rather sparse, so these generalizations should be considered approximate.

Below the soil horizons, heterotrophic bacteria are the dominant microorganisms. Organic matter that serves as carbon and energy source for aquifer bacteria is largely transported from the soil horizons. Autotrophic bacteria are relatively insignificant in aquifers, though they have been reported.

Introduction of xenobiotics to a pristine aquifer tends to disrupt the oligotrophic ecosystem. The net effect is a function of the xenobiotic, the ambient microbial community and hydrogeochemical conditions. Xenobiotics may stimulate microbial activity and dramatically increase microbial population density, or may be toxic to certain members of the population, or may have no effect at all. Microbial communities have an amazing capacity for adaptation to changing hydrogeochemical conditions, a trait that bodes well for their use as agents for in situ bioremediation.

Bacterial cells range in size from about 1 μm for well-fed, cultured organisms to approximately 0.1 μm for starved bacteria in a survival or dormant

mode (Ghiorse and Wilson 1988). Pore size in a silt or fine sand is of this same order of magnitude. Only compacted very fine-grained lithologies (e.g., clays) and tightly cemented or crystalline rocks (e.g., unfractured granite) have pore throats small enough to occlude bacteria.

Free or attached? Bacteria in the subsurface may be present as free-moving organisms, as sessile individuals or cell clusters, or may be embedded in a grain-coating film of organic polymer material (biofilm or slime). Unattached organisms may move passively with advective flow; motile organisms swim (e.g., with flagellae) in a random fashion or in response to external stimuli, such as chemical (chemotaxis) or thermal (thermotaxis) gradient. The consensus appears to be that most often microbes are attached, though direct observation is difficult and subject to sample preparation artifacts. A particular species may demonstrate different mobilities during different stages of its life cycle or as a survival mechanism in response to adverse environmental conditions. At least some microbes are mobile during some phase of their existence.

The question as to the mode of distribution and possible dispersal of micro-organisms has important implications in developing conceptual and mathematical models for microbial growth and substrate utilization, as well as for transport of pathogens. For example, biofilm models (Section 7.5) are predicated on the idea that bacteria are dispersed within a fixed organic film through which reactants and products must diffuse.

The potential for microbial mobility under natural or perturbed conditions clearly has significant implications for in situ bioremediation. Implementation of in situ bioremediation may require inoculating a soil or aquifer with contaminant-degrading microbes, perhaps genetically modified bacteria. For source area cleanup, these microbes either must be introduced in proximity to the contaminants or be capable of migrating toward the contaminants. Understanding microbial mobility may be important in the proper design of in situ bioremediation schemes.

Metabolic processes and energetics

Biotransformation reactions involving XACs and most other xenobiotic compounds are mediated by heterotrophic bacteria, which in order to survive, grow, and/or reproduce, require:

a. Carbon sources as primary substrates, e.g., sugars, acetate.

b. Electron donors for the oxidation half-reaction as an energy source; commonly also serve as the carbon source.

c. Electron acceptor(s) for the reduction half-reaction, e.g., O_2, NO_3^-, SO_4^{-2}.

d. Macronutrients, e.g., phosphate, nitrate.

e. Micronutrients, e.g., trace metals.

Limited availability of any one of these requirements can inhibit microbial processes. Additionally, of course, water is required as a medium of chemical transport, and environmental conditions (temperature, pressure, pH, ionic strength, contaminant levels, etc.) must be within microbial tolerance ranges. Extremes in environmental conditions do not preclude microbial activity; indeed certain species are highly adapted to particular extreme conditions. However, extremes may impact process rates. For example, the primary effect of lower temperatures is to retard degradation rates by slowing microbial metabolism. Although soil environments may be subject to extremes in temperature and water saturation, conditions are fairly stable in the deeper subsurface, below about 10-20 m.

A carbon source is essential for cell growth and reproduction. The carbon source may be a naturally occurring organic (e.g., acetate), the organic contaminant of interest, or a primary substrate introduced to enhance cometabolic reactions. The electron donor or reductant is typically an organic chemical which also serves as the primary substrate or carbon source, i.e., the carbon compound is oxidized.

The requisite energy for cell metabolic activity (e.g., respiration, cell growth and division, chemical transport, motility) is obtained through thermodynamically favorable, enzyme-mediated, oxidation-reduction (redox) reactions. Reactions involving a redox pair—electron donor and acceptor—generate the energy utilized by microbes. Electrons from the donor are transferred to the acceptor, typically through a series of intermediate reactions, any one of which may be rate-limiting. Many of these reactions, though thermodynamically favorable (i.e., involve a decrease in free energy; $\Delta G^o < 0$), are kinetically impeded by a high-energy transition state involved in the reaction; microbial enzymes serve to decrease this energy barrier and catalyze the reaction. The reaction may precede slowly or not at all in the absence of active microbes synthesizing the appropriate enzyme(s). The biotransformation reactions tend to be irreversible, though other microbes may mediate reactions that regenerate the original reactants (NRC 1990). Electron acceptors participate in the reduction half-cell reaction of the redox reaction. Common electron acceptors include oxygen (O_2), nitrate or nitrite (NO_3^-, NO_2^-), sulfate (SO_4^{-2}), and carbon dioxide (CO_2).

There are at least three classes of substrate (carbon/energy source) observed in biotransformation reactions, based primarily on microbial utilization: primary substrates, secondary substrates, and cometabolized compounds. How microbial populations utilize xenobiotics is central to the conceptual modeling of the reaction mechanism and stoichiometry, as well as developing appropriate mathematical descriptors for reaction kinetics and coupling of multiple reactions. Microorganisms tend to metabolize the solutes that provide the maximal energy return, assuming reaction-mediating enzymes

can be synthesized. Primary substrates are those compounds which microbes readily utilize as a carbon and/or energy source. A primary substrate is required for microbial growth and its availability strongly influences the rate of biomass growth.

Secondary substrates may also be utilized as a carbon or energy source, but their depletion does not measurably affect the net growth of bacteria. A substrate may be secondary because it is a less energetically favorable reactant or is simply present in too low a concentration to support growth. If primary substrates are depleted, secondary substrates may assume the role of primary substrate.

Cometabolic reactions are those mediated by microorganisms but from which they gain no carbon nor energy source. Cometabolism requires the presence of a primary substrate to support the metabolic activity. In situ biotreatment may involve introduction of primary substrates (and/or electron acceptors and nutrients) to stimulate microbial growth and cometabolism. For example, glucose, yeast extract, acetate, and biodegradable surfactants have been utilized as primary substrates to support TNT cometabolism. Cometabolic reactions may arise from the fortuitous release of reactive enzymes into the environment or to biofilm exopolymers during natural microbial processes such as division or lysis (cell rupture; death). Extracellular cometabolic reactions may alter the xenobiotic compound so that either the reaction product is rendered nontoxic to the microbe, or so that it may be utilized, perhaps by another bacterial group. Solutes affected by these relatively nonselective cometabolic reactions tend to be present in only trace concentrations. Cometabolism may be a significant microbial process affecting recalcitrant organic contaminants, including most XACs.

The reactivity of an organic substrate is a function of its composition and molecular structure and the ability of microorganisms to produce enzymes to mediate energetically favorable reactions. Xenobiotics with structures or · functional groups common in naturally occurring organics (e.g., C-C bonds, carboxyl, hydroxyl) tend to be more readily degraded, presumably since microbes are more likely to have evolved the ability to manufacture enzymes capable of utilizing these moieties. Nitrate groups and other electron withdrawing functional groups (e.g., halogens) on aromatics tend to inhibit bioreactions by deactivating electrophilic substitution (Pitter and Chudoba 1990, Kaplan 1993). If microorganisms could be cultured from soils in which simple nitroaromatics (e.g., nitrobenzene) or N-heterocyclic compounds (e.g., pyrrolidine or N-nitro-pyrrolidine) are being degraded, they may be useful in biotreatment of XAC-contaminated soils.

Phosphorous, nitrogen, and other nutrients are required for various metabolic processes. Iron, sulfate, phosphate, and nitrate concentrations are generally sufficient to support microbes in the typical oligotrophic aquifer (Ghiorse and Wilson 1988). If degradable xenobiotics are introduced via a contaminant plume at concentrations sufficient to induce biomass growth, phosphate or nitrate may become growth limiting, usually the former in fresh waters.

Sulfate too may be readily depleted, in which case methanogenesis may proceed. Nitrate and ammonia are present in some XAC plumes (e.g., Spalding and Fulton 1988) in which case the likelihood of nitrate limited growth is reduced.

Bacterial processes commonly proceed optimally within a finite range of conditions, being inhibited at both high and low extremes. Moderate concentrations of a xenobiotic may be optimal for utilization, whereas too high a concentration may be toxic, and too low a concentration may be insufficient to support use as a substrate. Data are sparse on optimal levels of requisite constituents, particularly with respect to XACs. Numerical modeling of condition-dependent processes is complicated and rarely attempted in practice because of our incomplete understanding.

Microbial metabolism may be very sensitive to concentrations of the key reactants, particularly as conditions approach rate-limiting status. This sensitivity must be appreciated in the development of mathematical descriptors and in the numerical solution of the nonlinear relations. Field-scale transport codes must capture advection-dispersion processes accurately in order to predict the reactant concentrations that microbial consortia will encounter. Molz and Widdowson (1988) warn that areal (two-dimensional) simulation of aerobic biodegradation involves the vertical averaging of concentrations, thereby numerically "mixing" oxygen introduced at the water table through the unconfined aquifer. Under diffusion-limiting conditions, such models will tend to overpredict aerobic biotransformation by missing the oxygen-limited conditions common within a bioreactive plume. Aquifer heterogeneities also tend to impede vertical diffusion of oxygen, another feature missed by most numerical models with block- or element-averaged properties.

Metabolic pathways. Microbial metabolism can be broadly classified as either aerobic or anaerobic. These terns also are applied in reference to the condition of a particular environment with respect to molecular oxygen. Molecular oxygen is required for obligate aerobes to function, i.e., oxygen is the only electron acceptor the bacteria can use. Obligate anaerobes require the effective absence of molecular oxygen, using other electron acceptors. Much of the soil environment, the vadose zone, and pristine, shallow aquifers are typically aerobic. Facultative anaerobes utilize oxygen when available and shift to other electron acceptors once oxygen is depleted. Pockets or microenvironments of anaerobic conditions may develop in fine-grained, organic rich, microbially active soils, so the two environments and associated bacterial populations are not mutually exclusive macroscopically (e.g., the numerical model discritization scale). Indeed, a commensal relation can develop between adjacent anaerobic and aerobic environments (and biotransformation reactions) to affect the degradation of recalcitrant compounds (e.g., McMahaon and Chapelle 1991, Chapelle 1992).

As a general rule, aerobic processes proceed faster than anaerobic processes, because the energy gain to the microorganism is greater for aerobic processes. In descending order of energy gain (the so-called energy tower),

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the common metabolic processes involve the reduction of oxygen, nitrate, manganese (Mn^{+4}), ferric iron (Fe^{3+}), sulfate, then carbon dioxide. Note the decreasing magnitude of the free energy change in this sequence in Table 7.1. Spatial variation in groundwater redox conditions associated with contaminant plumes have been observed to reflect this general trend in microbial metabolism (e.g., Lyngkilde and Christensen 1992). Note that respiration reactions involve inorganic compounds (e.g., O_2, Fe^{+3}, SO_4^{-2}) as electron acceptors, whereas fermentation reactions utilize organic compounds as the electron acceptors (Chapelle 1992).

Table 7.1
Representative Microbial Processes and Electron Acceptors (a Partial Listing of Microbial Diversity)

Metabolic Process[1]	Electron Acceptor	Reaction	Free Energy Change $(\Delta G^\circ)^2$ at pH 7 (kcal/equivalent)
Aerobic Reactions			
Respiration[B]	Oxygen, O_2	$CH_2O + O_2 \rightarrow CO_2 + H_2O$ (+salts)	- 29.9
Aerobic or Anaerobic Reactions			
Nitroaromatic Reduction	Nitrobenzene[3] (as example)	$CH_2O + C_6H_5 N_{[III]}O_2$ $\rightarrow CO_2 + Ar\text{-}N_{[-III]}H_2$	–
Nitrate Reduction	NO_3^-	$CH_2O + 0.5 N_{[V]}O_3^- + H^+ \rightarrow$ $CO_2 + 0.5 N_{[III]}O_2^- + 0.5 H_2O$	-19.6
Anaerobic Reactions			
Denitrification[B]	Nitrate, NO_3^-	$CH_2O + 0.8 NO_3^- + 0.8 H^+$ $\rightarrow CO_2 + 0.4 N_2 + 1.4 H_2O$	- 28.4
Manganese Reduction[B]	$Mn_{[IV]}$	$CH_2O + 2 MnO_2 + 2 HCO_3^- + 2 H^+$ $\rightarrow CO_2 + 2 MnCO_3 + 3 H_2O$	- 23.3
Ferric Iron Reduction[B]	$Fe_{[III]}$	$CH_2O + 4 Fe_{[III]}OOH + 4 HCO_3^-$ $+ 4 H^+ \rightarrow CO_2 + Fe_{[III]}CO_3 + 7 H_2O$	- 10.1
Sulfate Reduction[B]	$S_{[VI]}O_4^{2-}$	$CH_2O + 0.5 SO_4^= + 0.5 H^+$ $\rightarrow CO_2 + HS^- + H_2O$	- 5.9
Methano-genesis[B]	$C_{[IV]}O_2$	$CH_2O + 0.5 CO_2 \rightarrow CO_2 + 0.5 CH_4$	- 5.6

[1] Processes with superscript B from Bouwer (1992).
[2] ΔG° values from or calculated using methods described in Stumm and Morgan (1981).
[3] Ar - any aromatic structural unit; ΔG likely would vary with nature of AR and the position of the NO_2 group.

This microbial prioritization of metabolism has environmental significance in that one type of reaction tends to preempt the less energetic reactions. For example, nitrate reduction (denitrification) will not proceed measurably until oxygen is depleted, sulfate reduction rates are negligible until nitrate is used up, and so on. Each of these reactions may be mediated by different groups

of bacteria and may create discrete reaction zones within a contaminated aquifer.

Degradation pathways commonly involve a series of reactions metabolized by more than one microbial species under varying redox conditions. For large or complex molecules, these reaction pathways may be complex and ill-defined. Field verification presents a particular challenge. There are very little data on the multidimensional distribution of microbes, reactants, and products in the subsurface. For relatively recalcitrant xenobiotics, including many XACs, biotransformation is incomplete and the breakdown products may be as toxic as the original compounds or worse.

Several reviews of microbial metabolism and energetics are available (e.g., Atlas and Bartha 1987, Chapelle 1992, Harvey and Widdowson 1992, Hurst 1992). The process descriptors discussed here are generally applicable to any metabolic pathway, regardless of the specific components.

Microbial transport and mobility

Though most soil microbes are attached most of the time, some are motile or passively mobile during part or all of their lives. Transport of bacteria is important in groundwater remediation when degrading microbes must be transported to the contaminated zone or when migration induces biofouling. Process models to describe key aspects of microbial transport are in the developmental stage (Corapcioglu and Haridas 1984, 1985; Hornberger, Mills, and Herman 1992, Yates and Yates 1989). There is an apparent consensus as to what processes are important (see Table 7.2) and which system variables influence these processes, including:

a. Microbe properties: species, size, shape, cell wall or sheath properties.

b. Media structure: pore and throat dimensions.

c. System geochemistry: mineralogy (surface charge), ionic strength, pH, and temperature.

Mathematical models have been developed to describe various aspects of microbial or colloidal transport in porous media. However, most of these models rely on phenomenological parameters based on incompletely verified theory. Experimental data of sufficient thoroughness are rare. Model parameters may make sense but are not as yet uniquely quantifiable.

Passive transport. Particle transport models for porous media typically begin with the traditional advection-dispersion equation and add terms for immobilization (sorption, straining), entrainment, chemotaxis, and biomass growth and decay. Unattached microbes, like any small, suspended particles in water, show an apparent random motion in response to population density

Table 7.2
Summary of Processes Affecting Bacterial Transport in Porous Media[1]

Process		Description
Passive Transport	Advection	Microbes suspended in flowing water
	Hydrodynamic Dispersion	Dispersion (dilution) due to spatial variation in advective flow velocity through pore networks and heterogeneous media
	Brownian motion	Net, down-gradient, dispersion arising from random motion of individual particles; analogous to chemical diffusion
	Entrainment, Sloughing, or Declogging	General terms for transfer from attached or sessile condition to active transport
Active Transport	Chemotaxis	Up-gradient (positive) or down-gradient (negative) migration of motile bacteria in response to chemical gradients in nutrients or toxins
	Thermotaxis	Active response to thermal gradient
Immobilization or Deposition	Filtration, Clogging	Physical straining of cells in pore throats
	Sedimentation, Deposition	Settling from advective flow due to gravitational attraction
	Adsorption	Binding to solids by electrostatic or other mechanism; has been described with Freunlich isotherm

[1] From Corapcioglu and Haridas (1984, 1985); Yates and Yates (1988); and Hornberger, Mills, and Herman (1992).

gradients. The net effect is for the mass to diffuse down-gradient (Brownian motion).

Immobilization or deposition. Bacterial cell dimensions are on the same order of magnitude as pore throat diameters in sand and finer sediments. Mobile cells can be entrapped in a pore throat (filtration). Mobile cells may adhere to biofilms or mineral surfaces in response to changing hydrogeochemical conditions, including reduction in seepage velocity (sedimentation). Although most bacteria are of circumneutral buoyancy, larger cells may settle by gravitation to a surface. Changes in ionic strength or pH may affect electrostatic interactions between cell and mineral; very small bacteria may be electrostatically drawn to mineral surfaces. Microbial adsorption has been observed to fit a Freundlich isotherm more so than a Langmuir (Corapcioglu and Haridas 1984, citing Cookson 1970). Immobilization may also be part of a microbe's natural life cycle, a dispersal mechanism, or a survival response (if dormancy and mobility were initiated under low substrate conditions).

Active transport. There is no consensus as to the relative importance of active migration of bacteria in response to solute concentration (chemotaxis), temperature (thermotaxis), or other gradients. Taxis is difficult to demonstrate under laboratory conditions and is nearly impossible to resolve at the field scale. There is evidence that chemotactic microbes may have an advantage over other microbes in locating and utilizing substrates or avoiding toxics (Ford 1992, de Victoria 1989).

Microbe transport models. Corapcioglu and Haridas (1984, 1985) presented a mathematical model to describe the advection, dispersion, diffusion, deposition, entrainment, and biomass growth and decay of microbes in porous media. Numerous model parameters are proposed for which verification or unique quantification would be extremely difficult.

Hornberger, Mills, and Herman (1992) simplify the Corapcioglu and Haridas model by excluding biomass variation (growth, predation) in order to evaluate the effects of three control variables—microbe type, mineralogy, and ionic strength—on microbial transport:

$$\frac{\partial C_b}{\partial t} = \alpha_L \, (q/n) \, \frac{\partial^2 C_b}{\partial x^2} + (q/n) \, \frac{\partial C_b}{\partial x} + \left(k_e \, S_b - k_i \, C_b \right) \qquad (7\text{-}1)$$

where C_b is the suspended concentration of bacteria [cells·L_{pw}^{-3}; pw = pore water], and S_b is the "concentration" of immobilized bacteria associated with the solids [expressed in cells·L_{pw}^{-3}]. The last term in Equation 7-1 describes the change in S_b with time ($\Delta S_b/t$) due to entrainment (k_e; T^{-1}) and immobilization (k_i; T^{-1}). They report adequate (same order of magnitude) reproduction of one-dimensional breakthrough experiments with the simplified model. Coefficients to describe deposition varied in a consistent manner with grain/pore size, ionic strength, and organism. However, the entrainment and dispersion coefficients did not show a systematic variation with the three control variables. Column experiments by Scholl et al. (1990) suggest that ionic strength and porous medium mineralogy also influence bacterial transport.

7.2 Bacterial Growth Kinetics

Biotransformation kinetics are strongly dependent on bacterial biomass and viability. All models for xenobiotic transformation include, either explicitly or implicitly, some model for bacterial growth—either a static biomass (no net growth), or a dynamic system which requires a constitutive relation to describe the dependence of growth on substrate concentration or utilization rate. Substrate source strength is rarely constant, particularly in a remediation situation; therefore, growth and biotransformation reactions tend to be in a perpetual state of disequilibrium. Thus, there is a need for reliable and robust models for growth kinetics.

Numerous models have been proposed to describe the kinetics of growth, substrate utilization, and product generation. Descriptors range from strictly empirical to the theoretically rigorous and may involve consideration of the complex interactions between microbiology (type and abundance of micro-organisms), nutrient supply (electron sources and acceptors, C, P, and N sources), geochemical conditions (e.g., temperature, pH, Eh), and hydrogeo-logic setting (e.g., permeability and adsorptive properties of the medium).

Microbial growth kinetics (as well as microbial transport reviewed above) must be understood in order to predict and avoid biofouling of porous media, which can dramatically reduce permeability. In situ biotreatment technologies typically involve injection of nutrients (primary substrates and/or electron acceptors) at injection wells, which stimulates anomalous growth proximal to the borehole.

Monod growth kinetics

The Monod rate relation (Monod 1949) is a commonly used mechanistic model to describe the growth rate of a microbial population in a confined system under specified conditions. The growth rate is a nonlinear function of substrate concentration, asymptotic on a maximal rate:

$$\mu = \frac{\mu_{Max} \, C_S}{K_S + C_S} \tag{7-2}$$

where μ is the specific growth rate [cells·T^{-1}] which is asymptotic upon μ_{Max} as the growth-regulating, primary substrate concentration, C_S [M·L^{-3}], increases. Substrate concentration at $0.5\mu_{Max}$ is defined as the half-saturation constant, K_S [M·L^{-3}], which is interpreted as an indicator of the microbial ability to utilize the particular substrate (lower value more readily utilized). K_S values from 10 to 10^6 mg·L^{-1} have been reported and depend on both the microorganism and the substrate. A Monod expression for biomass growth is from Schmidt (1992):

$$\frac{d \, X_B}{d \, t} = \frac{\mu_{Max} \, C_S}{K_S + C_S} X_B \tag{7-3}$$

where X_B [M] is the biomass. The "specified" conditions mentioned above are as follows:

a. Required nonlimiting nutrients, i.e. other than C_S, are present in excess to meet metabolic requirements.

b. There are no physical barriers to impede transfer of substrates or metabolites to or from the microbes (e.g., intra-aggregate diffusion).

c. Optimal environmental conditions exist because model parameters will be sensitive to temperature or other variables. The Monod equation is analogous to the Michaelis-Menton equation for enzyme kinetics.

The Monod equation describes the influence of growth-limiting nutrients. At high substrate concentrations, $C_S >> K_S$, the growth rate, μ_{Max}, is constant and independent of small changes in the excess substrate concentration. At intermediate substrate concentrations, $C_S \approx K_S$, the growth rate is near 0.5 μ_{Max} and strongly dependent on changes in C_S. At very low substrate concentrations, $C_S << K_S$, the growth rate, μ, varies directly (perhaps linearly) with substrate concentration C_S, which may be depleted rapidly. The classical Monod model in Equation 7-2 does not account explicitly for the nongrowth nutrient requirements (to support cell maintenance, mobility, etc.), the impact of which may not be evident unless substrate concentrations are low. The Monod equation can be modified by adding a specific maintenance rate term, "$-m$" [cells·T^{-1}], to the right-hand side of Equation 7-2 (Schmidt 1992).

The Monod relation serves as a mechanistic model for bacterial growth under ideal conditions which are rare in nature, particularly in a soil or aquifer medium. The following are much more likely:

a. More than one of the required metabolic solutes is not present in excess.

b. Bacteria do not have unimpeded access to the requisite solutes.

c. Microbial populations are not pure, but rather a complex microbial ecosystem.

d. Xenobiotics or metabolic waste products which may be toxic to the organisms build up and impede growth.

None of these inconveniences are considered in the Monod model.

The initial substrate concentration (C_S^o) relative to the K_S is a significant influence on the subsequent growth and substrate utilization descriptors. Population increases exponentially by binary fission under unconstrained, ideal growth conditions, when C_S^o is significantly greater than K_S—logarithmic growth conditions. The number of cells as a function of time is $\ln N = k_g t + \ln N_0$ or $\log N = k_g t/2.3026 + \log N_0$, where k_g is the growth rate constant, and N_0 is the initial number of cells. For a constant rate of cell division, doubling time (t_{2x}) is $1/(1.4424 \, k_g)$ (Alexander and Scow 1989).

A logarithmic growth model describes biomass growth as an exponential function of biomass and assumes that no growth-limiting effects are operative. Such conditions could exist when a small initial population is exposed to a steady and excess supply of nutrients ($C_S^o >> K_S$). The growth rate would be μ_{Max}, and dX_B/dt would be $\mu_{Max} X_B$. The initially rapid growth rate will slow as substrate is consumed or the diffusion of nutrients and/or toxins

becomes rate-limiting. At low biomass levels substrate assimilation would be negligible due to the low activity. As bacteria numbers increase exponentially, the substrate would likewise disappear exponentially to zero, assuming equal activity for each individual.

A logistic model describes growth when the initial substrate level, C_S^o, is well below the K_S; substrate levels become increasingly growth-limiting. The differential form of the logistic growth equation is from Schmidt, Simkins, and Alexander (1985):

$$\frac{dX_B}{dt} = r_{Max} X_B \left[1 - \frac{X_B}{X_{Max}} \right]$$

(7-4)

where r_{Max} is the maximum specific growth rate, and X_{Max} is the limit to biomass (similar to carrying capacity). Integrating Equation 7-4 yields:

$$X = \frac{X_{Max}}{1 + \frac{X_{Max} - X_o}{X_o} e^{-rt}}$$

(7-5)

If X_B is much less than X_{Max}, then Equation 7-5 reduces to an exponential form: $X_B = X_B^o e^{-rt}$. As X approaches X_{Max}, growth becomes negligible. The logistic expressions have the advantage over the integrated Monod expression in that the logistic can be solved analytically, whereas the Monod must be solved numerically (nonlinear). The Monod model is more general but should be used only if it is needed to explain observed growth (Schmidt, Simkins, and Alexander 1985).

When microbial populations are first exposed to xenobiotics, there is usually a lag or acclimation period between the initial exposure and the development of enzymes to utilize the compound. The xenobiotic may also be toxic to a portion of the microbial community. Controls on the length of the lag period are poorly understood, and a priori estimates are required in bioremediation models that attempt to simulate the phenomenon. The lag period may extend indefinitely if other, more readily utilized, carbon or energy sources are available. Most models assume that the residence time of contaminants in the subsurface is great relative to the lag time and therefore assume an acclimated microbial population.

Growth in the presence of inhibitory substrates

Certain substrates that microbes may utilize at low concentrations are growth inhibiting or toxic at higher concentrations. This antimicrobial phenomenon may be incorporated in a modification to the Monod growth expression (Schmidt 1992):

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$$\mu = \frac{\mu_{Max} \, C_S}{(K_S + C_S) \left[1 + \dfrac{C_S}{K_I} \right]} \qquad (7\text{-}6)$$

where K_I is the inhibition constant. Commonly, Equation 7-6 is simplified to:

$$\mu_M = \frac{\mu_{Max} \, C_S}{K_S + C_S + \dfrac{C_S^2}{K_I}} \qquad (7\text{-}7)$$

which would be the case if $C_S >> K_S$ (Alexander and Scow 1989). Inhibitory behavior has been observed for several xenobiotics, including trichloroethene, phenol, and pentachlorophenol (de Victoria 1989, Klecka and Maier 1985, Rozich, Gaudy, and D'Adamo 1985). Traxler, Wood, and Delaney (1974) reports that TNT inhibited growth of bacteria at high concentrations (50 mg·L^{-1}), though it is transformed at low concentrations.

7.3 Biotransformation Kinetics

The dependence of growth and metabolic behavior upon variation in key substrates and nutrients is the basis for several biotransformation kinetic models. Alexander and Scow (1989) describe several types of microbial activity based on growth and substrate (or contaminant of concern) utilization; the activity of a particular microbial population may be as follows:

a. The microbial biomass grows and metabolizes the substrate (or contaminant) as a carbon, energy, and/or nutrient source; the substrate is required for growth.

b. Microbes grow utilizing a primary substrate (not the contaminant) while also mediating transformation of the contaminant; the contaminant is not required for growth but is either utilized as a secondary substrate (energy/carbon source) or cometabolized (not an energy or carbon source).

c. Microbes do not grow, but metabolize or cometabolize the contaminant.

Readily degradable xenobiotics may serve as a carbon source. More recalcitrant contaminants tend to transform by cometabolic processes if at all. The TNT biotransformation is generally a cometabolic process. In batch experiments, acetate, yeast extract, succinate, or other readily degraded organic is used as the primary substrate; all manner of organic matter is used as the primary substrate in composting. There are several reports of TNT being

utilized as a carbon, energy, and/or nitrogen source in pure cultures (e.g., Unkefer et al. 1990) but not in natural systems.

Empirical power function descriptors

Microbial transformation of organics under controlled conditions may be described by a generic power function:

$$\frac{d\,C_S}{d\,t} = -k_b\,C_S^{n_b} \tag{7-8}$$

where C_S is the substrate concentration [$M \cdot L^{-3}$]. The biotransformation rate constant k_b [units depend on the value of n_b] and the exponent n_b [–] are determined empirically by regression methods. If n_b is zero, then the kinetics are zero-order, and transformation proceeds at a constant rate regardless of concentration. First-order (or half-life) kinetics are described when n_b equals 1.0. Higher order kinetic expressions ($n_b > 1.0$) are commonly reported for soils. The fitted parameters of the power function model have no mechanistic implications, provide no insight as to controlling mechanisms, and thus present a rather weak basis upon which to make predictive estimates of biotransformations (Alexander and Scow 1989).

Monod-with-growth transformation models

A large family of substrate utilization models are based on the Monod growth concept (Simkins and Alexander 1984; Schmidt, Simkins, and Alexander 1985); see Figures 7.1 and 7.2. The differences are based on the relation between initial substrate concentration, C_S^o, and the half-saturation constant, K_S, by the nature of substrate use (growth substrate, cometabolite), and by the nature of bacterial population growth, if any.

Logarithmic kinetics. If the initial substrate concentration, C_S^o, is high relative to the saturation constant, K_S, and a single bacterial population is growing, the substrate disappearance may be expressed as:

$$\frac{d\,C_S}{d\,t} = -\mu_{Max}\left[C_S^o + X_B^o - C_S \right] \tag{7-9}$$

where X_B^o is the amount of substrate required to produce the initial population density. In integral form, Equation 7-9 is:

$$C_S = C_S^o + X_B^o\left[1 - e^{\mu_{Max}\,t} \right] \tag{7-10}$$
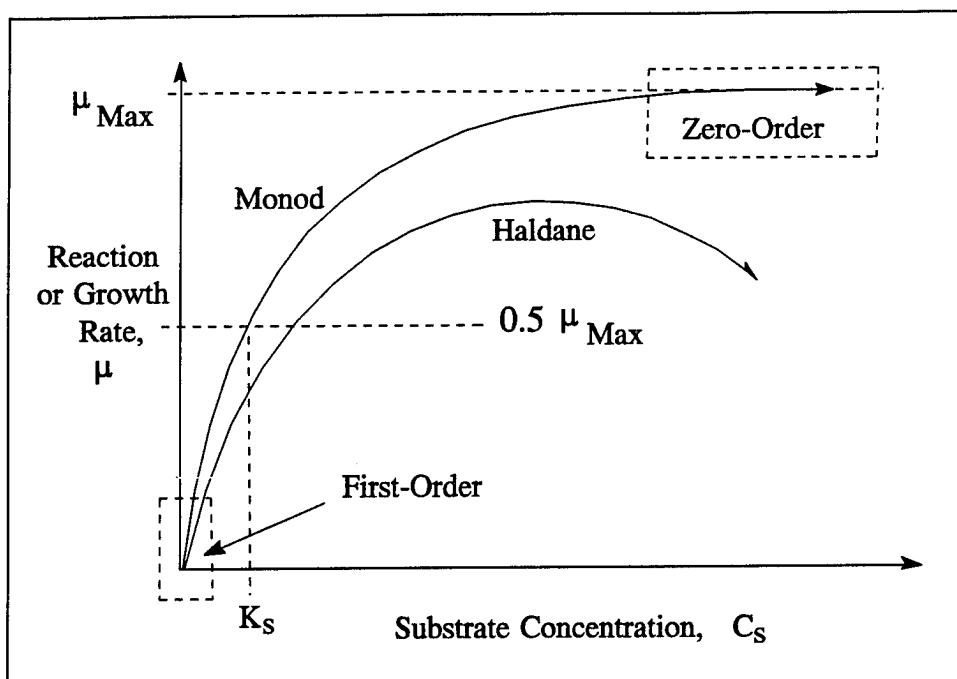
Figure 7.1. Substrate utilization rate as a Monod-type function of substrate concentration (note that first-order and zero-order kinetics are special cases of Monod kinetics)

Simkins and Alexander (1984). This style of kinetics may occur in special laboratory situations for degradable organics. Field concentrations of explosives solutes are typically very dilute and not likely to exceed the K_S value and may be inhibitory at moderate concentrations.

Logistic kinetics. Logistic growth kinetics may apply when the initial substrate concentration is much less than the half-saturation constant $(C_S^o \ll K_S)$. The differential form of the logistic kinetics is:

$$\frac{d\,C_S}{d\,t} = -k\,C_S\left(C_S^o + X_B^o - C_S\right) \tag{7-11}$$

where k is μ_{Max}/K_S. The integral form of Equation 7-11 is:

$$C_S = \frac{C_S^o + X^o}{1 + \left[\dfrac{X^o}{C_S^o}\right]\,\exp\left[k\,(C_S^o + X_0)\,t\right]} \tag{7-12}$$

(Simkins and Alexander 1984). Growth rates decrease with time as substrate is depleted. The logistic growth curve applies when both initial substrate concentration and microbial population density are low, which could be the case

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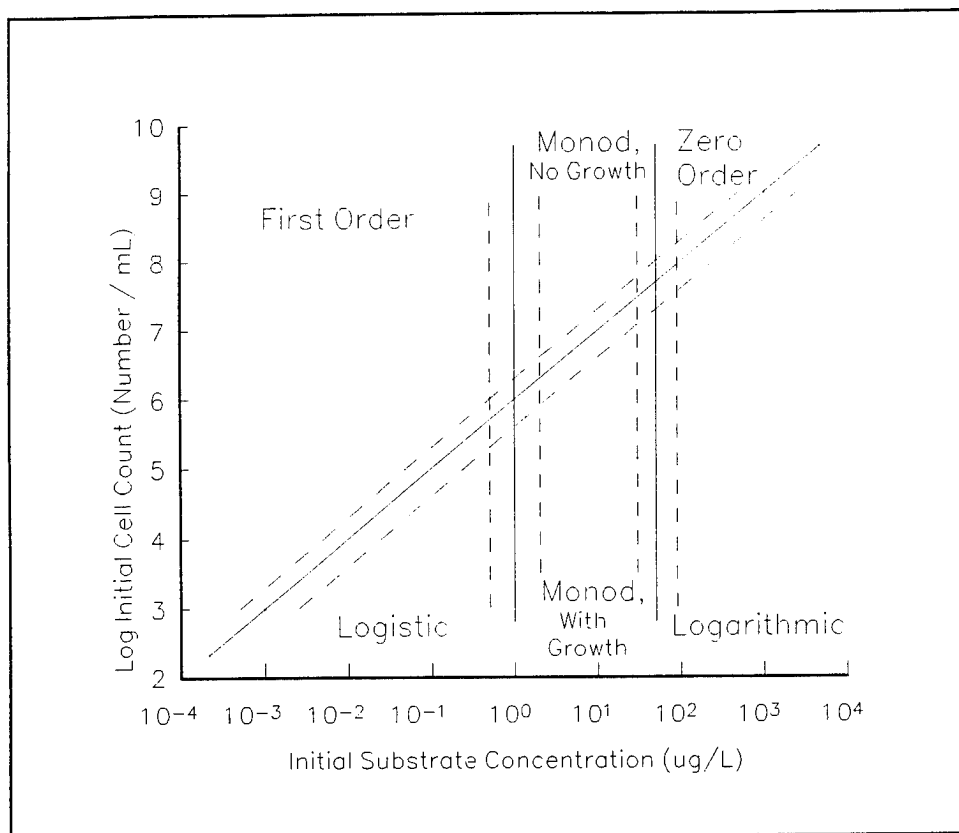
Figure 7.2. Monod kinetics models as a relative function of initial biomass and substrate concentration for a half-saturation constant of 1.0 (Field delineations by Simkins and Alexander (1984) represent the mineralization of (^{14}C) benzoate by a *Pseudomonas sp.* population under various initial conditions. Dashed lines ranges along boundaries indicate their nonspecificity.)

for typical oligotrophic aquifer systems. Schmidt, Simkins, and Alexander (1985) suggest that logistic kinetics may look linear during the time when the growth rate is between 10 and 90 percent of the maximum growth rate, though the tails are actually sigmoidal.

Monod-with-growth. When C_S^o is approximately equal to K_S, Monod-with-growth kinetics may apply as expressed by:

$$\frac{d C_S}{d t} = - \frac{\mu_{Max} C_S \left(C_S^o + X_B^o - C_S \right)}{K_S + C_S}$$ (7-13)

and the integrated form:

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$$ K_S \ln \left[\frac{C_S}{C_S^o} \right] = \left(C_S^o + X^o + K_S \right) \ln \left[\frac{X}{X^o} \right] - \left(C_S^o + X^o \right) \mu_{Max} \, t \quad (7\text{-}14) $$

(Simkins and Alexander 1984). This situation is a bit more complicated than the logarithmic or logistic kinetics, because of the more strongly nonlinear dependence of μ on substrate concentration. For logarithmic growth, μ is largely independent of substrate concentration, and for logistic growth, μ has a nearly linear dependence (see Figure 7.1). How appropriate this type of growth kinetics may be for explosives biodegradation is uncertain.

Haldane kinetics. Certain solutes can inhibit microbial processes when present at high concentrations, even though no deleterious effects are caused at low concentrations. The inhibitory effects on growth rate have been described with the Haldane modification of the Monod expression (Alexander and Scow 1989, Haldane 1930), which is presented in Equation 7-7 in the discussion of inhibitory substrates.

Monod-without-growth transformation models

Michaelis-Menten (no growth). Microbial populations may attain a steady-state growth condition when substrate concentration becomes stable. This condition is probably the norm in pristine groundwaters, where nutrient flux is low. Steady-state growth conditions may be approached at the margins of mature contaminant plume if the source is reasonably constant. In porous media, spatial limitations place a restriction on biomass growth even if nutrients are abundant.

When growth is limited or static, the observed biotransformation of substrate is conducted in the presence of a steady amount of enzyme (versus growth scenarios, where enzymes increase with biomass). Michaelis-Menten kinetics are predicated on the assumption of constant reaction constituents (enzymes) and have been applied to microbial processes in no-growth situations (Alexander and Scow 1989):

$$ k_m = \frac{K_{Max} \, C_S}{K_{S\,m} + C_S} \quad (7\text{-}15) $$

where k_m is the reaction rate [M·T^{-1}], K_{Max} is the maximum reaction rate [M·T^{-1}], and K_{Sm} is the Michaelis constant, analogous to the Monod half-saturation constant, K_S. The Michaelis-Menten is clearly similar to the Monod Equation 7-2; here the rate is for substrate reaction with a constant amount of enzyme, whereas the Monod expression describes a reaction with a rate that varies with biomass growth. As with the Monod-with-growth expression discussed above, the initial substrate concentration (C_S^o) relative to the Michaelis constant has a strong influence on the reaction kinetics.

Zero-order kinetics or linear biotransformation (no growth). When substrate concentration (C_S^o or C_S) is much greater than K_{Sm} (or K_S) and biomass (X_B) is constant, the rate of substrate loss is also constant. As long as the substrate concentration remains constant (excess), the rate of mass loss remains linear with time, thus this type of kinetics is called linear or zero-order. Zero-order kinetics without growth and $C_S^o \gg K_{Sm}$ (or K_S) may be expressed as:

$$\frac{d\,C_S}{d\,t} = - \left(\mu_{Max}\, X_B^o \right) = -k_{m\,1} \tag{7-16}$$

or as integrated:

$$C_S = C_S^o - k_{ml}\, t \tag{7-17}$$

(Simkins and Alexander 1984). Substrate loss occurs at a constant mass per time. Linear biotransformation kinetics are fairly common in soils. Substrate concentrations for which zero-order kinetics have been reported vary from 10^{-9} to 10^0 g·L^{-1}, thus representing values above and below their respective K_{Sm} values.

First-order kinetics (no growth). When $C_S^o \ll K_{Sm}$ (or K_S) and biomass is constant and large ($X_B^o >> C_B^o$), the substrate loss rate decreases with time as the substrate is consumed. Kinetics in which the rate is approximately linearly dependent on another variable (here, substrate concentration) are first-order with respect to that variable. First-order kinetics without growth may be as expressed by:

$$\frac{d\,C_S}{d\,t} = - \left[\mu_{Max}\, \frac{X_B^o}{K_{Sm}} \right] C_S = - \left(k_{m2} \right) C_S \tag{7-18}$$

or as integrated:

$$C_S = C_S^o\, e^{-k_{m2}\,t} \tag{7-19}$$

where k_{m2} is a first-order rate constant [T^{-1}] (Alexander and Scow 1989). First-order (or half-life) kinetics models are commonly utilized in contaminant transport models for convenience and ease of computation, as much as appropriateness. Rate constants are estimated easily by linear regression on *log* C_S versus time.

Although first-order kinetics have been reported for a number of contaminants, Alexander and Scow (1989) suggest that many of these claims are based on insufficient data to distinguish first-order kinetics from other models,

or fit the model poorly. Pseudo-first-order kinetics may arise from several scenarios (Alexander and Scow 1989):

a. Limiting nutrient or electron acceptor is available at a constant rate might be the case with O_2-diffusion limitation common in aerobic degradation within contaminant plumes.

b. A critical nutrient is exhausted, e.g., phosphate, required for a key enzyme.

c. Biomass already is large due to previous substrate loadings.

d. The solubility limit of the carbon source (or a critical nutrient) regulates supply after initial solute is exhausted.

Monod-without-growth. Substrate utilization under no-growth conditions may be described by Monod-without-growth kinetics when initial substrate concentrations are approximately equal to the Michaelis constant, $C_S \approx K_{Sm}$, (Alexander and Scow 1989):

$$\frac{d\,C_S}{d\,t} = -\frac{\left(\mu_{Max}\,X_B^o\right)\,C_S}{K_{Sm}\,+\,C_S} = -\frac{\left(k_{m3}\right)\,C_S}{K_{Sm}\,+\,C_S} \qquad (7\text{-}20)$$

or as integrated:

$$K_{Sm}\,\ln\left[\frac{C_S}{C_S^o}\right] + C_S - C_S^o = -\left(\mu_{Max}\,X_B^o\right)t = -k_{m3}\,t \qquad (7\text{-}21)$$

Monod type kinetics may be distinguished from first-order kinetics by conducting biodegradation experiments at several different initial substrate concentrations (Alexander and Scow 1989). Initial concentration-dependent rate constants determined by fitting a first-order model would be inconsistent with first-order kinetics, thus suggesting that Monod kinetics may be more appropriate.

Kinetics for organics not supporting growth

Schmidt, Simkins, and Alexander (1985) present twelve models (see Table 7.3) to describe the transformation kinetics of solutes that do not support growth, i.e., any growth is supported by a primary substrate, not the compound of interest. These models represent combinations of the four growth kinetics classes (logistic, exponential, linear, and no growth) and the three classes of substrate availability ($C_S << $, $\approx$, or $>> K_{Sm}$).

Model V fit 4-nitrophenol breakdown with a glucose substrate (Schmidt, Simkins, and Alexander 1985). Alexander and Scow (1989) observe that

Table 7.3
Twelve Models for the Transformation Kinetics of Solutes (S) Not Supporting Growth of the Active Organisms[1]

Model	Characteristics	Equation
Logistic Growth; any X_B		
I. Low C_S	Differential form	$-\dfrac{dC_S}{dt} = \dfrac{k_{1u}\, C_S\, X_{max}}{1 + (X_{Max} - X_B^o)\, e^{(-rt)}/X_B^o}$
	Integral form	$C_S = C_S^o \left[\phi(e^{rt} - 1) + 1\right]^{\frac{-k_{1u}}{r}}$
	Derived parameters	$\phi = X_B^o/X_{Max}$ and $k_{1u} = \mu_{Max}\, X_{Max}/K_m$
	Necessary condition	$C_S^o << K_m$
II. Intermediate C_S	Differential	$-\dfrac{dC_S}{dt} = \dfrac{\mu_{max}\, C_S}{(K_m + C_S)}\, \dfrac{X_{Max}}{1 + (X_{Max} - X_B^o)\, e^{(-rt)}/X_B^o}$
	Integral form	$K_m \ln(C_S/C_S^o) = [\phi(e^{rt} - 1) + 1]^{-k_{1g}/r}$
	Derived parameters	$\phi = X_B^o/X_{Max}$ and $k_{1g} = \mu_{Max}\, X_{Max}$
	Necessary condition	None
III. High C_S	Differential form	$-\dfrac{dC_S}{dt} = \dfrac{k_{1g}}{\left[(X_{Max} - X_B^o)/X_B^o\right]e^{-rt} + 1}$
	Integral form	$C_S = C_S^o - (k_{1g}/r)\ln[\phi(e^{rt} - 1) + 1]$
	Derived parameters	$\phi = X_B^o/X_{Max}$ and $k_{1g} = \mu_{Max}\, X_{Max}$
	Necessary condition	$C_S^o >> K_m$
Exponential Growth: $X_B << X_{Max}$		
IV. Low C_S	Differential form	$-\dfrac{dC_S}{dt} = k_1\, C_S\, e^{rt}$
	Integral form	$C_S = C_S^o \exp\left[-(k_1/r)\, [e^{rt} - 1]\right]$
	Derived parameters	$k_1 = \mu_{Max}\, X_B^o/K_m$
	Necessary condition	$C_S^o << K_m$ and $X_B << X_{Max}$
V. Intermed. C_S	Differential form	$-\dfrac{dC_S}{dt} = \dfrac{k_o\, C_S\, e^{rt}}{K_m + S}$
	Integral form	$K_m \ln\left[\dfrac{C_S}{C_S^o}\right] + C_S - C_S^o = -\dfrac{k_o(e^{rt} - 1)}{r}$
	Derived parameters	$k_o = \mu_{Max}\, X_B^o$
	Necessary condition	$X_B << X_{Max}$
VI. High C_S	Differential form	$-\dfrac{dC_S}{dt} = k_o\, e^{rt}$
	Integral form	$C_S = C_S^o - k_o(e^{rt} - 1)/r$
	Derived parameters	$k_o = \mu_{Max}\, X_B^o$
	Necessary condition	$C_S >> K_m$ and $X_B << X_{Max}$
		(Continued)

[1] Terms other than derived parameters are defined in text. Models adapted from Schmidt, Simkins, and Alexander (1985).

Table 7.3 (Concluded)

Model	Characteristics	Equation
Linear Growth: $X_B \approx 0.5\, X_{Max}$, fit to logarithmic curve in the 0.10 to 0.90 μ_{Max} range		
VII. Low C_S	Differential form	$-\dfrac{dC_S}{dt} = k_1\, C_S\, (1 + m\,t)$
	Integral form	$C_S = C_S^o\, \exp\left[-k_1(t + m\,t^2/2)\right]$
	Derived parameters	$k_1 = \mu_{Max}\, X_B^0 / K_m$
	Necessary condition	$X_B \approx X_{Max}/2 \quad and \quad C_S \ll K_m$
VIII. Intermed. C_S	Differential form	$-\dfrac{dC_S}{dt} = k_o\, C_S\, (1 + mt)/(K_m + C_S)$
	Integral form	$K_m \ln\left[\dfrac{C_S}{C_S^o}\right] + C_S - C_S^o = k_o\left[t + \dfrac{m\,t^2}{2}\right]$
	Derived parameters	$k_o = \mu_{Max}\, X_B^0$
	Necessary condition	$X_B \approx X_{Max}/2$
IX. High C_S	Differential form	$-\dfrac{dC_S}{dt} = k_0\, (1 + m\,t)$
	Integral form	$C_S = C_S^0 - k_0(t + m\,t^2/2)$
	Derived parameters	$k_0 = \mu_{Max}\, X_B^0$
	Necessary condition	$X_B \approx X_{max}/2 \quad and \quad C_S \gg K_m$
No Growth: $X_B \approx X_{Max}$		
X. Low S (First-Order)	Differential form	$-\dfrac{dC_S}{dt} = k_1\, C_S$
	Integral form	$C_S = C_S^o\, \exp\left[-k_1 t\right]$
	Derived parameters	$k_1 = \mu_{max}\, X_B^0 / K_m$
	Necessary condition	$C_S^0 \ll K_m \quad and \quad X_B^0 \approx X_{Max}$
XI. Intermediate C_S (Michaelis Menten)	Differential form	$-\dfrac{dC_S}{dt} = \dfrac{k_0\, C_S}{K_m + C_S}$
	Integral form	$K_m \ln(C_S/C_S^0) + C_S - C_S^0 = -k_0\, t$
	Derived parameters	$k_0 = \mu_{Max}\, X_B^0$
	Necessary condition	$X_B^0 \approx X_{Max}$
XII. High S (Zero-Order)	Differential form	$-\dfrac{dC_S}{dt} = k_o$
	Integral form	$C_S = C_S^0 - k_0\, t$
	Derived parameters	$k_0 = \mu_{Max}\, X_B^0$
	Necessary condition	$C_S \gg K_m \quad and \quad X_B \approx X_{Max}$

models I and IV describe well the breakdown of phenol by microbes growing on glucose but warn that application of these models to strictly cometabolic reactions has not been evaluated experimentally. The models with high C_S ($\gg K_{Sm}$) may not be applicable to cometabolism as mentioned earlier because the compounds may be inhibitory at high concentrations.

Mixed-order kinetics

Brunner and Focht (1984) propose a three-half-order kinetics model for biodegradation of carbon substrates in soil that may be pseudo-first-order (for no growth) or pseudo-second-order (with growth and concentration dependence). Two forms of the model are proposed: (a) for linear growth:

$$C_P = C_S^0 \left[1 - \exp \left[- k_1 t - \frac{k_2 t^2}{2} \right] \right] + k_0 t \qquad (7\text{-}22)$$

and (b) for exponential growth:

$$C_P = C_S^0 \left[1 - \exp \left\{ - k_1 t - \frac{E_0}{\mu} \left[\exp (\mu t) - 1 \right] \right\} \right] + k_0 t \qquad (7\text{-}23)$$

where C_P is the concentration of the reaction products such as a ^{14}C-labeled tracer [$M \cdot L^{-3}$], E_0 is the initial enzyme concentration, k_0 is a zero-order rate constant for the indigenous mineralization of soil organics or target substrate incorporated into soil humus [T^{-1}], k_1 is a proportionality constant [T^{-1}] related to degradation without growth, and k_2 is a proportionality constant [T^{-2}] related to the rate of increase in the first-order rate constant with time due to enzyme production (growth). If k_2 is zero (no growth), Equation 7-22 reduces to a first-order expression, plus the linear term for indigenous carbon sources.

The model requires no a priori estimates of reaction order, lag period, or corrections for endogenous mineralization. Brunner and Focht (1994) suggest several advantages of the three-half-order model over the Monod-based models: (a) fewer constants estimated by nonlinear regression (two versus four for the integrated Monod equation); (b) concentrations can be expressed as an explicit function of time; (c) biomass concentration data are not required; and (d) initial parameter estimates required for nonlinear regression analysis are easily determined from a linearized form of the descriptor. The mixed-order model seems to capture the acclimation phase (lag time) well for exponential growth scenarios. Capturing the lag period may not be important in the bioremediation of a mature plume remediation where microorganisms are already acclimated but may be useful in treatment design.

Brunner and Focht (1984) observe that exponential growth in soil media is not common (versus liquid medium) due to frequency of nutrient or substrate limitations or diffusion-related problems associated with soil aggregates or microbial masses (microcolony or biofilm). However, they report success in applying the exponential growth model to describe glucose degradation in soil

columns that had been gamma-irradiated to reduce the initial microbial population density.

Scow, Simkins, and Alexander (1986) suggest that models based on the Monod equation do not adequately describe the biodegradation kinetics of substrates at low concentrations in soils. The linear growth, three-half-order model best described most of their data for the mineralization of p-nitrophenol. A two-compartment model best fit the transformation of phenol (below 100 $ng \cdot g^{-1}$), aniline, and nitrilotriacetic acid. Schmidt, Simkins, and Alexander (1985) noted that Equations 7-22 and 7-23 are similar to models VII and IV in Table 7.3, except that the mixed-order model predicts substrate mineralization even in the absence of a metabolizing population.

Multiple substrate models

Microbial populations are typically capable of metabolizing several substrates, though they show a tendency to utilize the most energetically favorable substrates first. The Monod models for reactions controlled by a single substrate concentration, as those previously described, can be extended to describe situations in which multiple constituents are rate-limiting. Mathematical models to describe a multiple substrate system have primarily focused on dual-substrate systems, typically the biodegradable contaminant of concern and the electron acceptor involved in the bioreaction (e.g., O_2). Demonstrated cases in which multiple primary and/or secondary substrates simultaneously limit biotransformation reactions are few and tend to be too complex in natural settings to permit determination of model parameters (Schmidt 1992). Dual-substrate models have also been applied to cases of substrate inhibition, secondary substrate utilization, and cometabolism (Schmidt 1992).

Dual modified-Monod kinetic models. Borden and Bedient (1986) developed a dual modified-Monod kinetics model to describe the oxygen-limited biodegradation of petroleum hydrocarbons in porous media. This model serves as the basis for the two-dimensional (areal), BIOPLUME-II code (Rifai et al. 1987). Primary substrate concentration, C_S, utilization kinetics are described by:

$$\frac{d C_S}{d t} = - M_T K_{Max} \left[\frac{C_S}{K_S + C_S} \right] \left[\frac{C_O}{K_{SO} + C_O} \right] \qquad (7\text{-}24)$$

the electron acceptor (e.g., oxygen, O) kinetics by:

$$\frac{d C_O}{d t} = - M_T K_{Max} F \left[\frac{C_S}{K_S + C_S} \right] \left[\frac{C_O}{K_{SO} + C_O} \right] \qquad (7\text{-}25)$$

and the total, active microbial concentration, M_T [$M_{Bact} \cdot L^{-3}$], by:

$$\frac{d M_T}{d t} = M_T K_{Max} Y \left[\frac{C_S}{K_S + C_S} \right] \left[\frac{C_O}{K_{SO} + C_O} \right] + k_c Y C - b M_T \quad (7\text{-}26)$$

where K_{Max} [$M_S \cdot M_{Bact}^{-1} \cdot T^{-1}$] is the maximum substrate utilization rate per unit microbial biomass, K_{So} [$M \cdot L^{-3}$] is the half-saturation constant for oxygen, F is the stoichiometric ratio of oxygen to substrate consumed, Y [$M_{Bact} \cdot M_{substrate}^{-1}$] is the microbial yield coefficient, C [$M_{max} \cdot L^{-3}$] is the concentration of natural organic carbon (e.g., humic and fulvic acids), and b is the microbial decay (mortality) rate [T^{-1}]. It is not clear from the discussion by Borden and Bedient (1986) why the yield coefficient is the same for both the substrate (C_S, as in first term on right of Equation 7-26) and natural organic compound (C) which is typically more recalcitrant. The BIOPLUME—II model uses finite-difference for flow and a method-of-characteristics for transport, which includes sorption of substrate and electron acceptor by linear, Freundlich, or Langmuir isotherms and a variety of boundary conditions. MacQuarrie, Sudicky, and Frind (1990) also developed a dual-Monod bioremediation model.

Srinivasan and Mercer (1988) developed BIO1D, a one-dimensional model for aerobic or anaerobic degradation. Constant microbial biomass is assumed for steady-state conditions; the growth rate must adjust rapidly relative to advection of the substrate. In order to capture the effect of substrate or oxygen limitation on biotransformation, a dual-limited, modified Monod kinetics model is employed. Biomass is expressed as:

$$\frac{\partial C_S}{\partial t} = - M_T \mu_{Max} \left[\frac{C_S}{K_S + C_S} \right] \left[\frac{C_O}{K_{SO} + C_O} \right] \left[\frac{C_S - C_{S,Min}}{C_S} \right]$$

$$\text{For} \quad C_S \geq C_{S,Min} \quad \text{and} \quad C_O \geq C_{O,Min}$$

$$= 0 \quad \text{Otherwise}$$

$(7\text{-}27)$

where M_T is the microbial biomass [$M \cdot L^{-3}$], and $C_{S,Min}$ and $C_{O,Min}$ are the minimum concentrations of substrate and oxygen, respectively, needed to degrade the substrate [$M \cdot L^{-3}$]. Under anaerobic conditions, the last two bracketed terms in Equation 7-27 are dropped; under this Michaelis-Menten form of the equation, the anaerobic electron acceptor (e.g., nitrate, sulfate) is treated as nonlimiting (excess supply). The model may also be used to simulate secondary substrate degradation with a first-order rate expression ($C_S << K_S$).

Minimum-rate Monod. Often, one or more substrates is not present in excess, particularly in oligotrophic aquifers, and this absence or depletion

limits biotransformation. The limiting substrate is determined by the lesser of two rates; substrate use becomes:

$$\min \left\{ \mu_{Max\text{-}S} \left[\frac{C_S}{K_S + C_S} \right] , \ \mu_{Max\text{-}O} \left[\frac{C_O}{K_{SO} + C_O} \right] \right\} \qquad (7\text{-}28)$$

For substrate-limited biotransformation, the minimum-Monod model expression for substrate use becomes:

$$\frac{dC_S}{dt} = - M_T \mu_{Max\text{-}S} \left[\frac{C_S}{K_S + C_S} \right] \qquad (7\text{-}29)$$

whereas oxygen (or other electron acceptor) utilization is described by:

$$\frac{dC_O}{dt} = - M_T \mu_{Max\text{-}S} F \left[\frac{C_S}{K_S + C_S} \right] = F \frac{dC_S}{dt} \qquad (7\text{-}30)$$

and the expression for total microbial biomass concentration, M_T, is:

$$\frac{dM}{dt} = - M_T \mu_{Max\text{-}S} Y_S \left[\frac{C_S}{K_S + C_S} \right] + k_c Y C - b M_T \qquad (7\text{-}31)$$

(Odencrantz 1992). Note that the $\mu_{Max\text{-}S}$ and Y_S terms are specific for the substrate (C-source). F is a stoichiometry coefficient [$M_{Ox} \cdot M_S^{-1}$].

When microbial processes are electron acceptor-limited, the minimum-Monod equations are adjusted to the following expressions for electron acceptor (oxygen) concentration, C_O,

$$\frac{dC_O}{dt} = - M_T \mu_{Max\text{-}O} \left[\frac{C_O}{K_{SO} + C_O} \right] \qquad (7\text{-}32)$$

for substrate concentration, C_S:

$$\frac{d\,C_S}{d\,t} = -\,M_T\,\mu_{Max-O}\,\frac{1}{F}\left[\frac{C_O}{K_{SO} + O}\right] = \frac{1}{F}\frac{d\,C_O}{d\,t} \qquad (7\text{-}33)$$

and for total biomass concentration, M_T:

$$\frac{d\,M}{d\,t} = -\,M_T\,\mu_{Max-O}\,Y_O\left[\frac{O}{K_{So} + O}\right] + k_c\,Y\,C - b\,M_T \qquad (7\text{-}34)$$

(Odencrantz 1992). Note that now the μ_{Max-O} term is for the electron acceptor (oxygen).

The minimum-rate model assumes that either $\mu_{Max-s}\,C_s\,/\,[K_s + C_s]$ or $\mu_{Max-O}\,C_0\,/\,[K_{So} + C_o]$ controls the degradation rate. As guidance to whether the substrate or electron acceptor limit transformations, Williamson and McCarty (1976) and Rittmann and Dovantzis (1983) suggest that if the concentration ratio of electron acceptor to substrate is less than the ratio of the respective half-saturation constants:

$$\frac{C_A}{C_S} < \frac{K_A}{K_S} \qquad (7\text{-}35)$$

is true, then the electron acceptor concentration is rate-limiting (Equations 7-29 - 7-31); if false, then the substrate is rate-limiting (Equations 7-32 - 7-34).

Odencrantz (1992) compares dual-Monod and minimum-rate Monod formulations to determine under what conditions the two might produce disparate predictions. His formulations differ slightly from those of Borden and Bedient (1986) in the form of the background bacterial activity. Odencrantz includes a background microbial decay term ($+\,b\,M_{To}$), where M_{To} is the initial biomass concentration. This modification was suggested by Chiang, Dawson, and Wheeler (1989) to prevent excessive decay in the background cell concentrations for continuous source scenarios.

Odencrantz (1992) indicates that the two formulations are identical when both substrate (S) and electron acceptor (A) are in the zero-order range ($C_S \gg K_S$ and $C_A \gg K_A$). In the first-order range ($C_S \ll K_S$ and $C_A \ll K_A$) the two models are most disparate, the dual-Monod model predicting much lower reaction and growth rates. In the intermediate case of the hyperbolic range ($C_S \approx K_S$ and $C_A \approx K_A$) rates for growth and donor and acceptor utilization rates for the dual Monod are half those of the minimum-rate Monod.

7.4 Coupling to Partitioning-Limiting Processes

The natural subsurface is a complex heterogeneous environment in which multiple, interdependent, biogeochemical, and physical processes may be active. This interdependence or coupling is exceedingly difficult to resolve quantitatively, particularly with sparse field data. Bioavailability of XACs is coupled to dissolution and aqueous complexation or speciation (discussed below; Chapters 4 and 8), both chemical and physical sorption (Chapter 5), diffusion through microbial biomass (Section 7.5), and abiotic reactions (Chapter 8). Our understanding of the coupling between microbial processes and abiotic or other biotic processes is in the research stage of development, particularly for XACs.

Desorption- or dissolution-limited biotransformation

Organic contaminants not in aqueous solution commonly are assumed to be unavailable for biotransformation reactions, at least those which require transport across a cell membrane. The nonaqueous phase may be a strongly adsorbed state or a separate contaminant phase such as crystalline XAC, in which case any biotransformation reaction rates may be limited by desorption or dissolution kinetics, respectively. Both equilibrium and kinetic models for desorption or dissolution have been advanced to describe their potentially rate-limiting effects on biotransformation. One cleanup scheme for XACs and other sparingly soluble contaminants involves enhancing their bioavailability by increasing their aqueous solubility or partitioning with water-soluble surfactants and/or cosolvents. Microbial transformation of solubilized (desorbed or dissolved) may create conditions favorable for continued solubilization (Le Châtelier's Principle).

van Genuchten and Wagenet (1989) develop a suite of analytical solutions to describe first-order kinetic degradation within either a two-site sorption (kinetic and equilibrium) or a two-region (mobile-immobile water) model. Degradation kinetics may be independent of association (mobile or immobile region, solute or sorbate condition); thus there may be as many as four rate coefficients for the two-region model and as many as three for the two-site model. The two-site and two-region solutions are of identical form when expressed in dimensionless parameters, though definitions of parameters vary. Gamerdinger, Wagenet, and van Genuchten (1990) apply the two-site/two region model to describe degradation of pesticides.

Angley et al. (1992) investigate equilibrium versus nonequilibrium desorption coupled with biotransformation in one-dimensional column experiments and simulations. Nonequilibrium desorption as the rate-limiting factor fits the observations of the aerobic degradation of alkylbenzenes better than did simulations with an equilibrium assumption. A first-order expression appeared satisfactory to describe biotransformation only in solution and without an acclimation period.

McBride et al. (1992) investigate the biotransformation and sorption kinetics of quinoline (a two-ring, N-heteroaromatic). They observe less quinoline retardation (earlier breakthrough) in column breakthrough experiments in the presence of quinoline-degrading, microbial activity than in abiotic columns (not inoculated). This apparent inconsistency is not resolved, but speculation is offered for contributors to the phenomenon: (a) quinoline is displaced by competitive sorption with metabolites, primarily two-hydroxy-quinoline; or (b) biomass covers quinoline sorption sites in the clay-coated solids. These speculative processes are considered too minor to account for the observed disparity; they may be worthy of consideration in modeling XAC sorption behavior.

Dissolution kinetics for sparingly soluble compounds, such as most XACs, to aqueous solution could limit bioavailability. Malone, Kao, and Borden (1993) develop a model to couple nonaqueous phase liquid (NAPL) dissolution kinetics with biotransformation. They demonstrate that a first-order kinetic expression for dissolution fits observations better than an equilibrium partitioning assumption. There are very little data relating dissolution kinetics of solid contaminants to bioavailability.

Multicompartment physical-chemical models

Physical and chemical heterogeneities in soils may induce microbial heterogeneities, e.g., very fine-grained aggregates in a soil or aquifer system may be physically inaccessible to bacteria, but not to solute molecules passing through the advective matrix. Conversely, anaerobic microenvironments within a matrix of aerobic conditions may develop in organic-rich soils; here the anaerobic activity is active only within the aggregate, and obligate aerobic processes are precluded.

Soil bacteria diameters range between 0.5 and 1 μm (Casida 1971, Alexander and Scow 1989), whereas 50 percent or more of the pore space in soils is below 1 μm (Cary and Hayden 1973). However, it is the relatively narrow pore throats (rather than pore diameters) that restrict microbe transport, consistent with the observation that bacteria tend to occupy pore spaces of diameter greater than 2 μm (Kilbertus 1980).

The departure of transformation kinetics in soils from Monod-based kinetic models is likely due to the common violation of the assumption that bacteria have unrestricted access to substrates. Molecular diffusion into (or out of) immobile water zones could impose a rate limitation on transformation. Several conceptual models have been advanced to describe coupling between biotransformation processes and rate-limiting substrate supply.

Physical, two-compartment, biotransformation models have been proposed (e.g., Scow, Simkins, and Alexander 1986, Scow and Alexander 1992) that are analogous to the dual-region, mobile-immobile water, or two-site sorption models described previously (Chapter 5). Two compartments are defined on

the basis of bioavailability (the ease of substrate utilization). The high utilization compartment includes zones where bacteria have easy access to nutrients, as might be the case for low-density, bacterial populations in high permeability zones. A second compartment represents the xenobiotic present in areas less accessible to bacteria. These reservoirs, as they will be referred to here, may be conceptualized as: (a) adsorbed, (b) trapped in low permeability zones, or (c) present as a discrete phase (crystalline XAC or immiscible organic liquid).

The two-compartment model of Scow, Simkins, and Alexander (1986) includes four, first-order, rate constants—two for mass transfer into (k_1) and out of (k_2) the reservoir compartment (subscript 2), and two for biotransformation in the bioaccessible region (k_3) and in the reservoir region (k_4). The general conceptual model may be described as:

$$Products \overset{k_3}{\leftharpoonup} C_1 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_2 \overset{k_4}{\rightharpoonup} Products \tag{7-36}$$
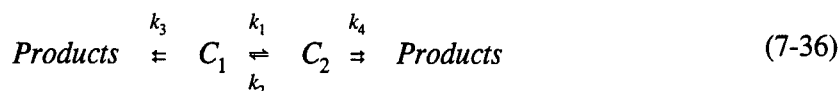
If biotransformation in the reservoir is neglected, a common assumption, $k_4 = 0$. The k_1 and k_2 rate constants may describe, respectively, sorption and desorption, dissolution and precipitation, or diffusive loss or gain to the bioaccessible region. The processes in Equation 7-36 may be described mathematically as:

$$\frac{d\,C_1}{d\,t} = -\left(k_1 + k_3 \right) C_1 + k_2 \; C_2 \tag{7-37}$$

and

$$\frac{d\,C_2}{d\,t} = k_1 \, C_1 - \left(k_2 + k_4 \right) C_2 \tag{7-38}$$

Scow, Simkins, and Alexander (1986) report that the two-compartment model or the linear, mixed-order (3/2) model best fits the data from mineralization of low concentrations of phenol nitriloacetic acid. Scow and Hutson (1992) and Brusseau, Jessup, and Rao (1989, 1992) present models to describe coupling between biotransformation and two-region, multiprocess nonequilibrium sorption.

Transport of nutrients or other process requirements (e.g., electron acceptors) to regions of microbial transformation may also be diffusion-limited and constrain biotransformation. This transport is very common in established, bioactive, contaminant plumes, in which aerobic degradation is active at the

plume margins, but negligible within the plume due to O_2 limitations (Molz and Widdowson 1988).

7.5 Biomass Diffusion Models

Conceptual models of the physical distribution of microbial biomass in porous media typically envisage one of three scenarios: (a) microbes occur as dispersed individual cells, (b) microbes grow in discrete patches or micro-colonies; or (c) microbes form a semi-continuous layer or biofilm of exopolymer material (see Figure 7.3). Contaminants, microbes, and nutrients must converge to the same proximity in order for biotransformation reactions to proceed, particularly if microbial uptake is required. Thus, the distribution of microbes in the subsurface has bearing on how the system is described mathematically and parameterized in practice. The latter two conceptualizations above necessarily involve the molecular diffusion of reactants and products between the bulk porewaters and the microbes within the biomass.

Early workers designing trickle filtration systems for wastewater treatment discovered that substrate diffusion into and out of microbial biomass imposed a limit on degradation rates. The bacterial biomass in these systems develops over the support materials, sometimes large cobbles, and forms a mat or film of exudate (slime) in which the microbes are imbedded. Molecular diffusion through the microbial biomass is recognized as a rate-limiting process in these biofilm reactors. The same conceptual model has been applied to subsurface systems, though the concept of even a thin continuous biofilm in soil or aquifer porous media is counterintuitive.

The oligotrophic nature of most subsurface environments (below uppermost soil horizons) is inconsistent with abundant microbial biomass. Direct observations (e.g., by scanning electron microscopy) in natural porous media are rare and subject to interpretation. However, the data suggest that microbes occur in small patches or clusters. The microcolony concept is an attempt to approximate these observations.

Both the microcolony and biofilm modeling approaches are limited by the difficulty in independent parameter verification (e.g., biomass distribution). In practice, parameter assignment becomes a fitting exercise, and either approach can yield results consistent with observations. Baveye and Valocchi (1989) compared models based on the biofilm, microcolony, and Monod "bulk" distribution concepts. They recommended that, due to the nonunique parameters in the biofilm and microcolony models, the Monod model is preferable. Baveye and Valocchi (1989) and Rittmann (1993) suggest that there is no effective difference between microcolony and biofilm approaches other than conceptualization of the model parameters. The same set of observations can be matched with either approach.
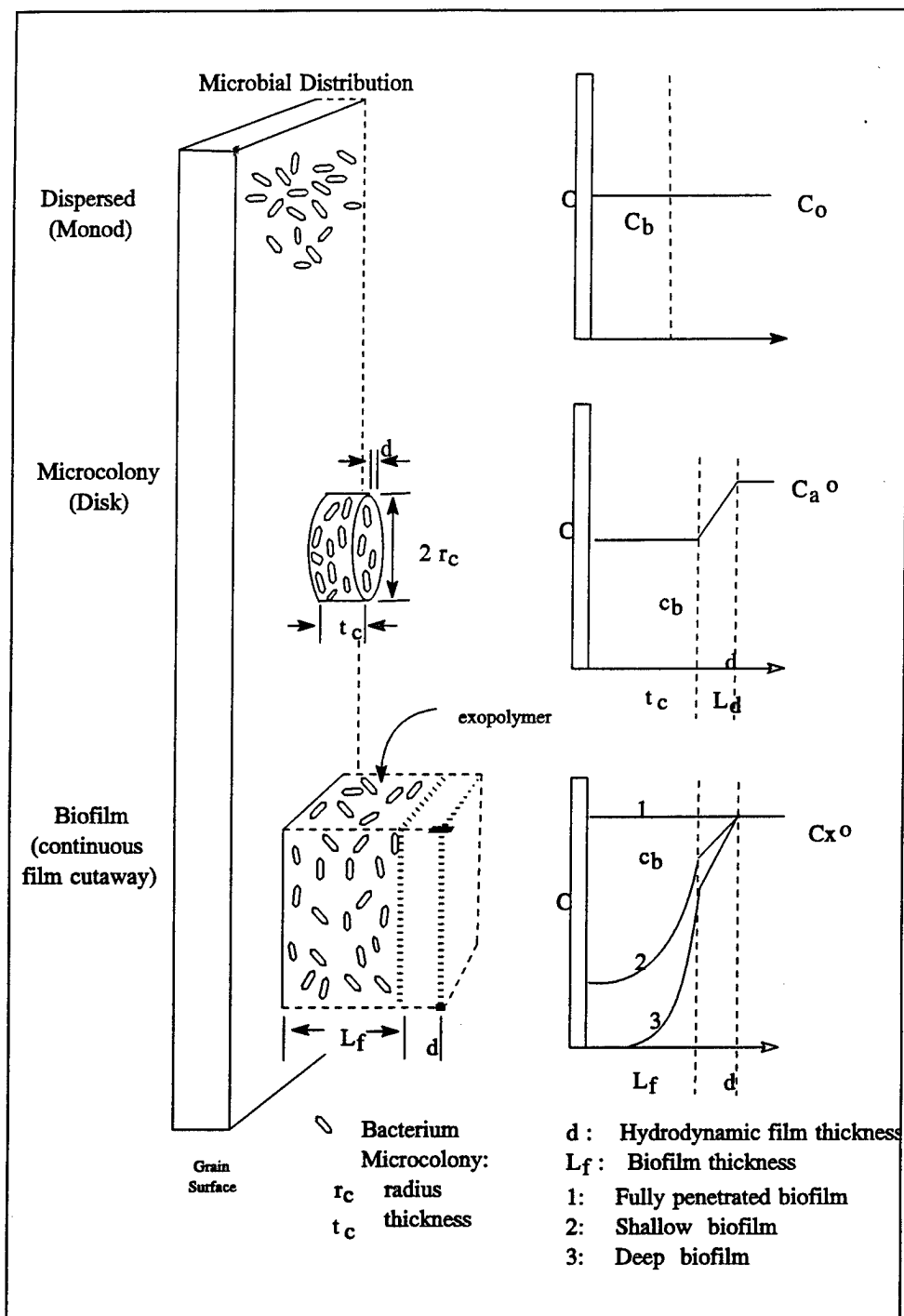
Figure 7.3. Three conceptualizations of microbial biomass distribution in the subsurface (after Odencrantz, Valocchi, and Rittmann 1990)

Microcolony models

Microcolony models (Molz, Widdowson, and Benefield 1986, Widdowson, Molz, and Benefield 1987, 1988, Chen et al. 1992) are based on the conceptualization that bacteria occur in small clusters (microcolonies) of 10 to 100 cells (Harvey, Smith, and George 1984), into which substrates (carbon and energy sources), electron acceptors, and nutrients must diffuse (see Figure 7.3). The Molz, Widdowson, and Benefield microcolony models approximate biomass as disk-shaped with an average colony radius of r_c [L] and thickness of τ_c [L]. Thus, for a number N_c microcolonies per unit volume of porous medium, the average biomass volume would be $N_c \tau_c \pi r_c^2$.

Molz, Widdowson, and Benefield (1986) and Widdowson, Molz, and Benefield (1987, 1988) employ a modified-Monod model to describe growth and substrate utilization kinetics and capture the potential growth-limiting effects of substrate, electron acceptor, or both. Substrate decay and electron acceptor utilization are incorporated as a sink term in the transport equations of a one-dimensional, Eulerian-Lagrangian, finite difference, numerical model which also simulates advection, dispersion, sorption (linear), and biomass changes (colony proliferation or decay).

Solutes (substrates, electron acceptors, wastes) must diffuse through an hydrodynamic boundary layer of thickness δ [L] between the pore water and microcolony (see Figure 7.3). At the steady-state conditions evoked by the model, solute α utilization rates per colony, r_α [M·T^{-1}], are equal to diffusive fluxes and:

$$r_S = D_{sb} \left[\frac{C_S^o - c_S}{\delta} \right] \pi r_c^2 \qquad (7\text{-}39)$$

for substrate, and:

$$r_O = D_{ob} \left[\frac{C_O^o - c_O}{\delta} \right] \pi r_c^2 \qquad (7\text{-}40)$$

for oxygen, where D_{sb} and D_{ob} are the boundary layer diffusion coefficients [L^2·T^{-1}] for substrate and oxygen, respectively. In these and subsequent biomass diffusion expressions, a lower case c_α refers to concentration of species α associated with the biomass (colony or films), and an upper case C_α refers to open porewater concentrations. Subscripts s and o refer to substrate and oxygen, respectively. Diffusion is considered only at the disk top surface, not at the disk sides, in the Molz, Widdowson, and Benefield (1986) version.

Chapter 7 Biotransformation

Assuming a modified-Monod kinetics (dual-limitation), the substrate utilization rate, r_S [M·colony^{-1}·T^{-1}], may be described as:

$$r_S = \frac{\mu_{Max} m_c}{Y} \left[\frac{c_S}{K_S + c_S} \right] \left[\frac{c_O}{K_O + c_O} \right] \qquad (7\text{-}41)$$

where Y is the specific yield [dimensionless; $M_{bact}·M_s^{-1}$], and m_c is cell mass per colony [M]. Gross biomass production, $Y r_s$ [M·T^{-1}], from the carbon source substrate is defined by multiplying Equation 7-41 by Y.

Oxygen (or electron acceptor) utilization is described in terms per colony for both biomass synthesis ($Y r_s$ term below; r_s defined in Equation 7-41) and maintenance (respiration) with modified-Monod kinetics:

$$r_O = \gamma Y r_s + \alpha k_{md} m_c \left[\frac{c_O}{K_O' + c_O} \right] \qquad (7\text{-}42)$$

where γ is the dimensionless (–) oxygen use coefficient for synthesis, α is the oxygen use coefficient for maintenance (–), k_{md} is the microbial decay coefficient [M·M^{-1}·T^{-1}], and K_O' is the oxygen saturation constant for decay [M·L^{-3}].

Microbial biomass growth is treated by increasing the number of colonies (N_c) rather than the size of the colonies. The macroscopic equation for biomass growth and decay is:

$$\frac{1}{N_c} \frac{d N_c}{d t} = \mu_m \left[\frac{c_S}{K_S + c_S} \right] \left[\frac{c_O}{K_O + c_O} \right] - k_{md} \qquad (7\text{-}43)$$

The model does not consider variation in microcolony size, microbial inactivity, or microbe mobility.

Widdowson, Molz, and Benefield (1988) extended the Molz, Widdowson, and Benefield (1986) model to include nitrate-reduction, possible nitrate-limitations on growth, and ammonia-N as a potentially limiting nutrient. Thus, any of four components may limit bacterial processes—substrate (carbon or energy source), electron acceptors (oxygen or nitrate), or nutrient (ammonia). The disk-shaped microcolony concept is modified slightly to include diffusion into the sides of the colonies; total surface area for diffusion (β) is now ($\pi r_c^2 + 2\pi r \, \tau$). The new model, however, utilizes an effective surface area for diffusion on a per biomass or per colony basis rather than colony geometry assumptions. Two additional mass transfer expressions are

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required to describe the exchange of nitrate and ammonia between porewaters and colonies: 1) for nitrate (subscripted N):

$$r_N = D_{Nb} \left[\frac{C_N - c_N}{\delta} \right] \frac{\beta}{m_c} \qquad (7\text{-}44)$$

and 2) for ammonia (subscripted A):

$$r_A = D_{Ab} \left[\frac{C_A - c_A}{\delta} \right] \frac{\beta}{m_c} \qquad (7\text{-}45)$$

To capture the inhibitory effects of colony oxygen on anaerobic nitrate-reduction, an inhibition factor (I_o) is introduced:

$$I_O = \left[1 + \frac{c_O}{K_c} \right]^{-1} \qquad (7\text{-}46)$$

where K_c is the inhibition coefficient [$M \cdot L^{-3}$]. The set of equations solved are similar to those described above for the 1986 model, with added Monod factors for ammonia and nitrogen limitation and the inhibition factor affecting nitrate utilization. Widdowson, Molz, and Benefield (1988) also note that a remediation scheme based on nitrate as an electron acceptor is less impeded by supply limitations than is the case with aerobic degradation because nitrate is much more soluble in water (50-100 mg$\cdot$L^{-1}) than is oxygen (typically less than 9 to 12 mg$\cdot$L^{-1}).

Biofilm models

Biofilm models conceptualize the microbial biomass as a continuous layer of bacteria and associated exopolymers, completely covering soil or aquifer solids. Bacteria are uniformly distributed through the film of uniform thickness L_f [L] with biomass density X_f [$M \cdot L^{-3}$]. Solute flux is calculated only in the direction (z) normal to the solid surfaces, passing through both a hydrodynamic boundary layer of thickness δ and then into the microbe-bearing film (see Figure 7.3).

Numerous biofilm models have been developed, differing with respect to the complexity in the film structure and numerical methods employed to solve the nonlinear governing equations. Biofilm models applied to porous media typically adopt relatively simple models, such as the "fully penetrated" or thin biofilm model (McCarty, Rittmann, and Bouwer 1984) in which steady-state concentration gradients are established relatively quickly (e.g., Baveye and

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Valocchi 1989). Kissel, McCarty, and Street (1984), Bouwer and Cobb (1987), Rittmann and McCarty (1981) and others present biofilm models.

Biofilms up to 100's of microns thick may develop provided sufficient space is available. Chemical gradients across the thin boundary layer would be relatively small compared to that across a thick biofilm. Generally, the thicker the biofilm, the more stratified and heterogeneous the biofilm becomes, and the more difficult to describe mathematically. Fortunately, thick biofilms in porous media, if they exist, appear to be rare phenomena, associated with special situations such as additive (substrate, electron acceptors, or nutrients) injection systems for in situ bioremediation efforts.

Biofilm processes and their descriptors are complicated because of the simultaneous diffusion and bioreactions involved. A steady-state mass balance expression on the biofilm substrate concentration, c_{sf} [M·L^{-3}], with reaction and diffusion over biofilm depth (z) expressed by Odencrantz, Valocchi, and Rittmann (1990) as:

$$D_f \frac{\partial^2 c_{sf}}{\partial z^2} = k_m \frac{X_f c_{sf}}{K_s + c_{sf}} \tag{7-47}$$

where D_f is the molecular diffusion coefficient in the biofilm [L^2·T^{-1}], k_m is the maximum specific rate of substrate utilization [M·M^{-1}·T^{-1}], and X_f is the concentration of active biomass [M·L^{-3}]. The D_f value is typically $0.8D_m$, the molecular diffusion coefficient of the constituent (Odencrantz, Valocchi, and Rittmann 1990). The concentration profile can be treated as steady state so long as the profile adjusts quickly to any changes in biofilm thickness or small changes in conditions.

The diffusive mass flux of substrate, J_s [M·L^{-2}·T^{-1}], through the boundary layer of thickness L_d may be described with Fick's second law:

$$J_s = D_m \frac{C_s - c_s}{L_d} \tag{7-48}$$

where C_s is the substrate concentration in the bulk liquid, and c_s is the substrate concentration at the biofilm-boundary layer interface. Odencrantz, Valocchi, and Rittmann (1990) adopt an operator-splitting approach to calculate advective-dispersive transport equations separately from the highly nonlinear biofilm transformation kinetics. In their comparison of Monod and biofilm model predictions, they conclude that molecular diffusion and external mass transfer in biofilm model did not have a strong influence on the plume or biomass distribution.

Baveye and Valocchi (1989) describe a biofilm model that may be applicable to porous media in which the film is sufficiently thin to be "fully penetrated" by solutes, i.e., assumed to be homogeneous in terms of the solute concentrations the bacteria utilize. This biofilm model at steady state is mathematically equivalent to the microcolony model. Baveye and Valocchi (1989) assert that the biofilm, microcolony, and "strictly macroscopic" (Monod type kinetics), for similar conditions, are mathematically similar (though conceptually quite distinct), and thus any can be fit to a particular set of data.

The appropriateness of biofilm models for porous media is rather questionable. Some utility has been gained in applications to simulate biofouling, but any model in which an increase in biomass decreases porosity could be used. The biofilm model evolved out of the water treatment discipline and was designed for nutrient rich, well-mixed, even turbulent, systems (e.g., trickling filters), where biofilms could reach thicknesses of several hundred microns (Siegrist and Gujer 1985). There is direct evidence of bacteria occurring in large clusters (Vandevivere and Baveye 1992a,b), but the classic concept of a biofilm has not been observed in natural, porous media, except perhaps in organic rich soils. A continuous film is not observed even in the case of bio-fouled media in the field, such as gravel packs and adjacent media associated with nutrient injection wells, or under controlled laboratory conditions with cell counts up to 10^{10} cells cm^{-3} (Vandevivere and Baveye 1992a,b). Calibration of a biofilm model involves adjusting the film thickness; calibrated thicknesses may be less than the thickness of a single bacterium.

A comparison of Monod and biofilm kinetics models by Odencrantz, Valocchi, and Rittmann (1990) suggests that at the field scale neither the plume nor the biomass distributions are sensitive to simulation of molecular diffusion. Thus, if the biofilm conceptual model is valid for porous media, the added complexity may not be practical for most remediation design.

It is likely that in typically heterogeneous porous media that local microbial buildup will be a self-regulating process, i.e., biomass may grow to the point that impedes advective transport, but in so doing, the flux of substrates and nutrients is diverted, preventing further growth. Much more fundamental research is needed to delineate the distribution of microorganisms in aquifers and soils.

7.6 Hydrodynamic Effects of Biomass

Bacterial growth in porous media can reduce the permeability of the medium by reducing porosity and occluding pore throats (Taylor and Jaffé 1990a, 1991; Vandevivere and Baveye 1992a,b,c). The problem of porous media biofouling has received considerable attention recently and is reviewed here briefly. Vandevivere and Baveye (1992a,b,c) experimented with four strains of bacteria and found that slime producers could dramatically reduce permeability, whereas the other strains produce lesser impacts.

Taylor and Jaffé (1990a,b,c, 1991) developed a biofilm model to describe the hydrodynamic effects of bacterial growth in porous media, primarily proximal to injection wells (nutrients, electron acceptors) for in situ bioremediation technology. The Taylor-Jaffé model embraces the biofilm model as a conceptual basis to simulate not only biotransformation and biomass growth, but also advective biomass transport and the hydrodynamic effects of biomass growth. Their model includes a feedback to predict hydrodynamic effects from biofilm growth effects on porosity, permeability, and longitudinal dispersivity. Taylor, Milly, and Jaffé (1990) evaluate several descriptors for the permeability reduction effects of biomass (biofilm) growth. Baveye, Vandervivere, and de Lozada (1992) criticize Taylor and Jaffé for presuming the validity of the biofilm conceptual model without sufficient justification.

Corapcioglu and Haridas (1984, 1985) describe the effects of microbial transport and growth. The hydrodynamic effects of biomass growth is related primarily to porosity-reduction. Baek, Clesceri, and Clesceri (1989) model biodegradation in unsaturated media, including the hydrodynamic effects of bacterial growth. They make the analogy of bacteria transport to clays transport, since they are approximately the same size. However, this analogy is limited, since the environmental controls on the transport of clays and bacteria are likely quite different.

Biofouling of near well-bore zones is a special problem for which innovative solutions must be found, such as pulsing the feed of substrate and/or nutrient or alternating electron acceptors. The potential for biofouling in column experiments evaluating biotransformation suggests that columns should be constructed with sample ports through which hydraulic head could be monitored. Development of locally strong pressure gradients may suggest biofouling. The potential for microbe filtration suggests that studies on in situ biofilm development in soil or aquifer material (versus inoculating the medium with endogenous organisms) should begin with homogeneously inoculated column rather than introducing an endogenous culture at inflow end.

7.7 Explosives Biodegradation

Evidence is abundant that explosives and associated compounds (XACs) are susceptible to biotransformation (Rosenblatt et al. 1989, McCormick, Cornell, and Kaplan 1976, 1978, 1981, Kaplan 1993), but that biodegradation typically is limited. Soil composting, a cleanup technology based largely on microbial degradation, has been applied to XAC-contaminated soils with apparent success (TNT concentrations reduced). Natural in situ biotransformation is likely to contribute to the fate and transport of XACs in several cases of aquifer contamination (ETA 1991a,b, Spalding and Fulton 1988). Most field investigations where biodegradation is suspected, based on XAC disappearance, are poorly documented in terms of measuring spatial and temporal variations in key variables such as probable primary substrates, electron acceptors, nutrients, biomass (e.g., numbers, enzymes, DNA), reaction products, etc.

The TNT and RDX have been the focus of most biotransformation research on XACs. Virtually all of this work has been related to soil or groundwater ex situ treatment, not in situ biotransformation. Natural in situ biotransformation of nitroaromatics appears to be dominated by a series of nitro-to-amino reduction reactions. The subsequent reactions are less well understood.

Two general biotransformation pathways have been observed for nitroaromatics, including TNT: a) sequential nitro-to-amino reduction, and b) elimination of the nitro group to form nitrite. By far, the most commonly reported reactions involve the nitro-to-amino reduction in which the nitro groups are utilized as electron acceptors or cometabolites. Nitro-to-amino reductions are observed for both aerobic or anaerobic conditions, though the reaction may be enhanced under anaerobic conditions. This pathway generates mono-, di-, and perhaps tri-amino products. Aromatic amines are subject to a number of reactions including polymerization, covalent binding to soil organics, and complexation (see Chapter 8). Biotransformation is typically incomplete under laboratory conditions, though high degradation efficiencies have been reported; Kaplan (1993) presented a recent summary of biotreatment research.

The elimination or cleavage of nitro groups from nitroaromatics is mediated by microorganisms or consortia that mineralize the compounds, utilizing them as the sole source of carbon, energy, and/or nitrogen (Schackmann and Müller 1991, Boopathy and Kulpa 1992, Pruess, Fimpel, and Diekert 1993). This reaction pathway has been reported for laboratory experiments with cultured (Boopathy and Kulpa 1992; Pruess, Fimpel, and Dikert 1993) or genetically modified (Duque et al. 1993) microorganisms. Conditions may be aerobic or anaerobic. No reports of field evidence for microbially mediated elimination are available at present.

TNT biotransformation

TNT is susceptible to biotransformation and partial mineralization under both aerobic and anaerobic conditions (Kaplan 1993). Predominant biotransformation products are amino- and diamino- compounds formed by nitro group reduction to an amino group through a hydroxamite intermediate, as depicted in Figure 7.4. (Kaplan and Kaplan 1982). Several azo and azoxy compounds also have been identified as products of TNT biotransformation (McCormick, Cornell, and Kaplan 1978, Kaplan and Kaplan 1982, Kaplan et al. 1985, Kaplan 1993). Confirmed reaction products include the following:

- 2-amino-4,6-dinitrotoluene.

- 4-amino-2,6-dinitrotoluene.

- 2,4-diamino-6-nitrotoluene.

- 2,6-diamino-4-nitrotoluene.
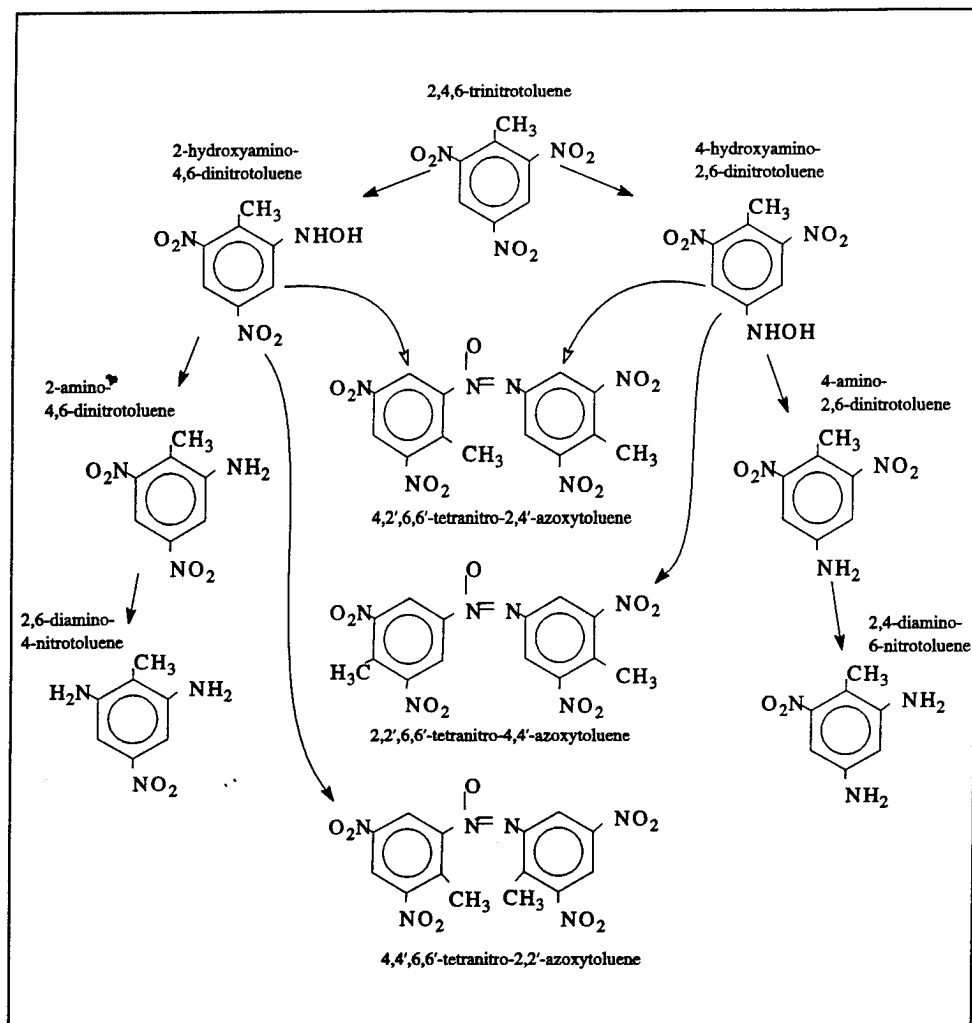
Figure 7.4. Reductive biodegradation for TNT (modified from Kaplan and
Kaplan (1982) and Kaplan (1993))

- 2′,4,6′,6-tetranitro-2,4′-azoxytoluene.

- 2,2′,6,6′-tetranitro-4,4′-azoxytoluene.

A reaction pathway proposed by McCormick, Cornell, and Kaplan (1978) and
Kaplan and Kaplan (1982) includes hydroxamite compounds which were not
detected analytically:

- 4-hydroxylamino-2,6-dinitrotoluene.

- 4,4′,6,6′-tetranitro-2,2′-azoxytoluene.

- 2-hydroxylamino-4,6-dinitrotoluene.

The difficulty in detection suggests that if these intermediates do form they are
highly transient.

The amino-aromatic biotransformation products of TNT can polymerize into recalcitrant azoxy or azo compounds, particularly under anaerobic conditions. Since polymerization does not appear to occur under aerobic conditions, it appears that redox conditions strongly influence XAC fate and transport. The anaerobic nitro-to-amino reduction reactions mediated by the nitroreductase enzyme system are nonspecific (Kaplan 1993).

Kaplan and Kaplan (1982) conducted biotreatment studies using ^{14}C-radiolabeled TNT in compost material. In addition to biotransformation they report significant binding to soil humus fractions which tends to increase with aging: 1.3 percent of recovered radioactivity at 24 days versus 13.9 percent at 91 days. Between 5.7 and 22 percent of the TNT became associated with the soil organic fraction and was not extractable with ether, ethanol, water, or acetone. The absence of ^{14}C-active volatiles suggests that no mineralization occurred.

Naumova et al. (1988) report that for TNT nitro-reduction reactions, nitrate is a more effective electron acceptor than oxygen—100 percent versus 66 percent reacted, respectively—in the first reduction to monoamino compounds. However, oxygen is more effective than nitrate as an electron acceptor in the second nitro reduction to form diamino compounds—85 percent versus 69 percent reacted, respectively. The authors suggest that this fact accounts for the predominance of monoamino metabolites under anaerobic conditions and diamino metabolites under aerobic conditions. These observations also suggest that a mixed aerobic-anaerobic environment, as in an organic-rich soil with anaerobic microenvironments, might be most effective in reducing TNT.

Schackmann and Müller (1991) examine aerobic bioreduction of TNT and other nitroaromatics by various *Pseudomonas* species. They observe the usual monoamino and diamino metabolites. Nitro reduction reactions are common in aerobic soils and may be mediated by a variety of pseudomonades. The authors report a TNT conversion rate of 0.5 mmol·L^{-1}·h^{-1} by *Pseudomonas sp.* CBS3 cultured on 4-chlorobenzoic acid as a carbon source. The same rates of reduction were observed for both aerobic and anaerobic conditions (argon atmosphere).

Kanekar and Godbole (1984) report that several varieties of soil bacteria from a site long contaminated with TNT could affect TNT disappearance. They report 15 to 63 percent removal by *Pseudomonas trinitrotoluenophila*, *Citrobacter freundi*, and *Bacillus polymyxa*. Bausum, Mitchell, and Major (1992) report nearly complete biodegradation of 2,4-dinitrotoluene and 2,6-dinitrotoluene by bacteria from contaminated surface waters. They contend that under laboratory conditions both 2,4-DNT and 2,6-DNT may serve as a carbon and energy source. They report that up to 64 percent of substrate carbon is converted to $^{14}CO_2$ with a concomitant increase in biomass.

TNT may be biotransformed and partially mineralized by fungi such as the lignin-degrading white rot fungi *Phanerochaete chrysosporium*. Fernando,

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Bumpus, and Aust (1990) report significant mineralization of ^{14}C-labeled TNT by *P. chrysosporium* in both liquid and augmented soil cultures. They observe as much as 85 percent TNT loss after 90 days from soils with 10 g/kg TNT.

RDX biotransformation

Only anaerobic biotransformation of RDX has been identified. McCormick, Cornell, and Kaplan (1981) identified the following anaerobic biotransformation products derived from low concentrations of RDX:

- Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine.

- Hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine.

- Hexahydro-1,3,5-trinitroso-1,3,5-triazine.

- 1,1-dimethylhydrazine.

- 1,2-dimethylhydrazine.

- Hydrazine.

- Formaldehyde.

- Methanol.

Experiments with ^{14}C-labeled RDX showed no active volatiles. Spanggord et al. (1980a,b) stimulated anaerobic biotransformation of RDX in sediments using yeast extract as a primary substrate. Sikka et al. (1980) report complete disappearance of RDX from activated sludge by anaerobic biodegradation with CO_2 generation. A proposed anaerobic reaction pathway is depicted in Figure 7.5 (Kaplan 1993).

The proposed degradation pathway proceeds via a series of anaerobic nitro-to-amino reductions until destabilization and fragmentation of the ring occur. Some of the reaction products are highly toxic (e.g., hydrazine). Aerobic biodegradation of the reaction products has been proposed for treatment but redox conditions would be a challenge to control in the subsurface.

7.8 Summary and Research Recommendations

Biotransformation appears to play a major role in the subsurface fate of explosives. The most common biotransformations reported for explosives are the sequential reduction of nitro to amino moieties. Nitro group elimination reactions and subsequent mineralization of TNT and other nitroaromatics are

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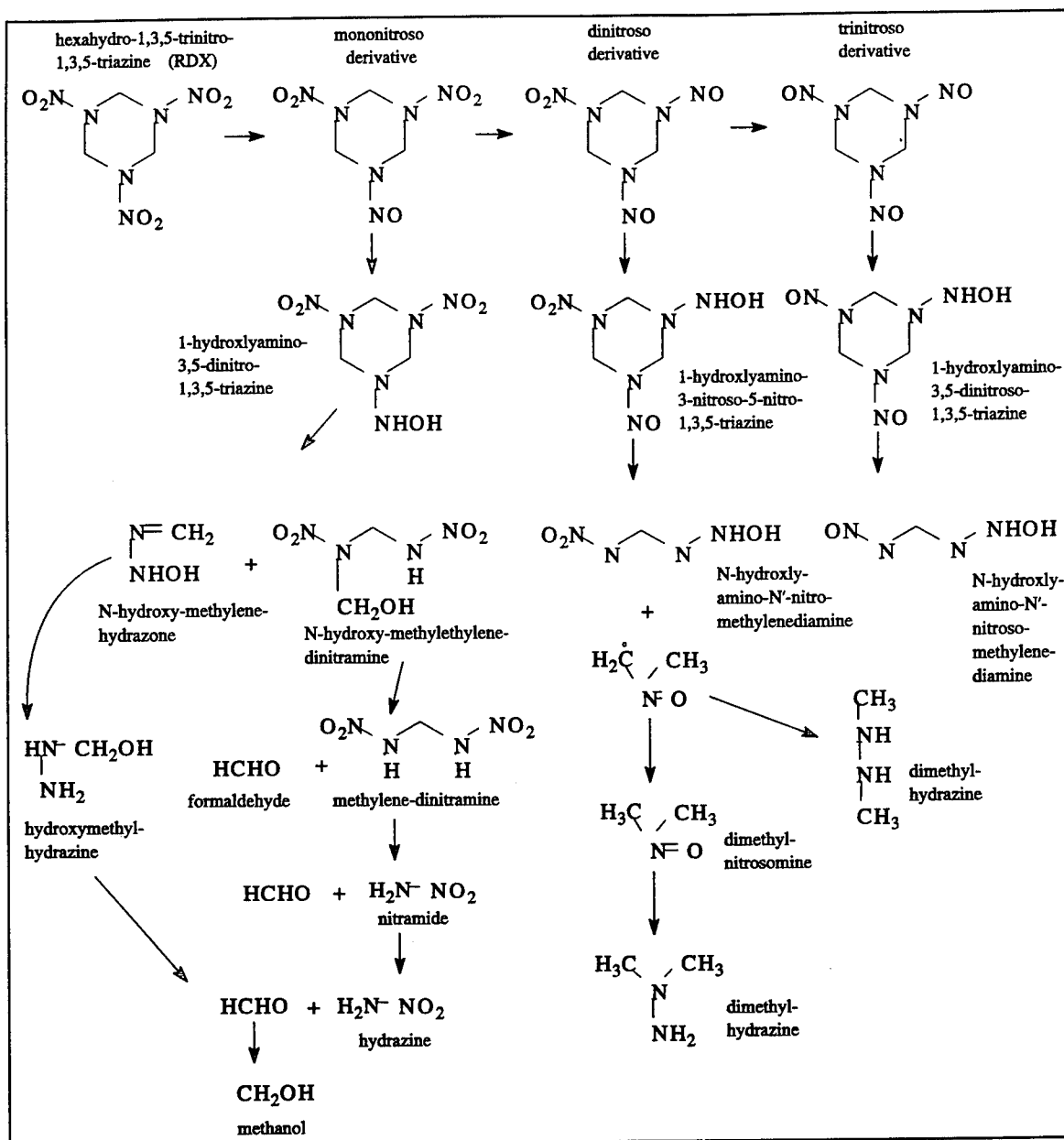
Figure 7.5. RDX anaerobic reaction pathway (after Kaplan (1993))

also reported. TNT undergoes these reduction reactions under aerobic or anaerobic conditions. RDX appears to undergo the reduction reactions only anaerobically. The presence of a readily degradable carbon/energy source (cometabolite) is necessary for explosives degradation, though TNT-supported growth under controlled conditions has been reported.

The general biotransformation pathways for TNT, RDX, and a few other explosives are reasonably well established. However, the kinetics of the intermediate steps and overall reactions are poorly known. Application of first-order transformation kinetics in the simulation of explosive transformation in

groundwater contaminant transport studies should be considered a preliminary estimate and without justification beyond observation matching.

Development and application of mathematical descriptors for the microbial transformation of explosives and XACs require knowledge or informed estimates regarding the following:

   a.   The conditions for biotransformation or mineralization, including:

      (1)   Minimal and optimal concentrations for substrates, electron acceptors, and nutrients to support desired bioreactions.

      (2)   Concentrations of XACs or any additives at which inhibitory phenomena may develop.

   b.   The reaction mechanism, involving:

      (1)   The stoichiometry of the complete reaction and intermediate reactions.

      (2)   Reaction kinetics, including identity of any rate-limiting, intermediate reaction(s).

   c.   Coupling to other processes, particularly:

      (1)   Abiotic reduction and soil binding reactions.

      (2)   Physical nonequilibrium sorption.

   d.   The influence of chemical and environmental variables on reaction kinetics, mechanism, and biomass growth that is needed to optimize in situ remediation.

   e.   The long-term fate of biotransformation intermediate products.

Establishing the identity of the microbial consortia members and/or active enzyme systems would be extremely useful for remediation engineering but is not essential for numerical modeling.

Recommendations for research

Several knowledge gaps identified below present serious impediments to bioremediation technology applied to explosives and numerical modeling in support of bioremediation design and optimization.

Identify relative importance of microbial versus abiotic reduction reactions. The relative influence of biotic versus abiotic reactions (Chapter 8) is arguably *the major question at the present time* regarding the fate of

explosives in the subsurface. Reaction products of these two mechanisms are similar; however, reactants, kinetics, and controlling variables surely differ. This question is as much of a concern in treatment design (e.g., composting) as it is in fate and transport modeling (natural attenuation) or risk analysis.

To investigate bioreactions in natural soils, the abiotic reactions must be controlled or "shutdown" in experiments parallel to unmodified soils. Evidence for microbial degradation of explosives is based largely on experiments conducted in aqueous or culturing media. Evidence of XAC biotransformation in soils is less unequivocal—disappearance of reactants, appearance of products—observations that could be obscured by abiotic reactions. Biotic reactions in bench-scale experiments can be retarded by a variety of chemical or irradiative means. Until the abiotic reactions are identified any shutdown of these reactions will be simply fortuitous. Direct evidence such as biomass changes (cell counts or enzyme assays) are needed.

Support through chemical analyses in field and laboratory investigations. The principal shortcoming in much XAC biotransformation research has been the incomplete tracking of reactants and products (XACs, primary and secondary substrates, electron acceptors, etc.). Insufficient data are particularly problematic at the field scale where these data become prohibitively expensive to acquire and have not been a high priority for site cleanup. Standards for the intermediate compounds (e.g., the amino compounds) have only recently become available and are prohibitively expensive for routine chemical analyses. For all fate research involving explosives, however, these intermediates should be included in the analysis scheme.

Establish environmental controls on biotransformation kinetics and pathways. The overall biotransformation reactions for TNT, RDX, and a few other explosives appear to be reasonably well established (e.g., Figures 7.4 and 7.5). However, the kinetics of the degradation pathways and the variety of possible environmental controls on those kinetics are poorly understood. More research is required to establish environmental controls on the biotransformation of explosives. The effects of temperature and aqueous geochemistry (inorganic as well as organic) on degradation pathways and rates are only qualitatively known. These controls must be better understood in order to design and implement more effective remediation strategies and to increase the likelihood that laboratory determinations will be useful in the field where conditions are not so readily controlled. It may be that field-scale bioreaction kinetics appear pseudo-first-order, but there is no a priori reason for this to be the case always, and blind application without justification is dangerous. Intrusive in situ remediation technologies may disrupt the first-order tendencies.

The complete mineralization in situ of most explosives is not demonstrated, though it may be possible under controlled laboratory conditions (Kaplan 1993). Continued research on enhanced biotreatment will eventually identify the optimal mix of microorganisms (consortium), substrates, and nutrients to

maximize mineralization. Transferring this technology to the subsurface for in situ bioremediation presents a whole set of new challenges.

Develop a numerical model for explosives biotransformation. A single, universally applicable model is not yet available to predict XAC biotransformation in realistically complex field situations with multiple, interacting substrates and bacteria. Many general advection-dispersion groundwater transport codes include simple biotransformation reactions, usually assuming first-order decay kinetics. Research and commercial codes specifically designed for bioremediation modeling typically invoke some form of Monod kinetics, but only for primary substrates. Research continues toward identifying appropriate conceptual models for microbial distribution (biofilm versus microcolony versus dispersed), the controls on microbe dispersal, the specific mechanisms and energetics of biotransformation reactions, environmental controls, and coupling of bioreactions to other subsurface processes. There is little consensus in most of these research areas, particularly with respect to the complex biochemistry of XACs.

Development of an in situ bioremediation code for application to explosives should be a very high priority in light of the attractiveness of this remediation option and because biotransformation appears to be one of the major subsurface processes affecting XACs. No commercial bioremediation code currently available is sufficiently complex to model explosives biotransformation and transport except at a most rudimentary level. Table 7.4 summarizes and prioritizes the features required for explosives biotransformation modeling. Three classes of modeling are identified—minimal, better, and research. Codes meeting the minimal requirements are probably available at present but were not designed for atypical contaminants such as explosives. The "adequate" classification suggests the number of enhancements needed to begin to model the biotransformation of explosives seriously. This level of code should be made available to the Army user community as soon as possible. The "research" level of code development is, as the name suggests, more complex, designed to evaluate processes in a much more rigorous manner, but perhaps too complicated for general application because of limited data availability. This list only hints at other processes that are unique to explosives which are recommended elsewhere for inclusion in a general, multiprocess model for explosives.

Table 7.4
Suggested List of Minimal, Adequate (Preferable and Deliverable), and Research Level Characteristics for In Situ Biotransformation Code Development

	Minimal	Adequate	Research
Flow			
Saturation Condition	Saturated	Variably Saturated	Variably Saturated; multiple, constitutive relations options
Dimensions	2-D	3-D	3-D
Transport Equations			
Explosives	1 constituent	2-5 constituents	4-10 constituents; most sites ident have only 1-2 explosives in the source wastes
Reaction Intermediates or XACs	0	2-4	4-10; depends on number of initial solutes
Primary Substrates	0-1 (assume excess)	2 (additives and/or background)	2-3 (multiple additives, background, perhaps XAC)
Electron Acceptors (EA)	1 (oxygen)	2 (oxygen, nitrate)	2-6 (also XAC-NO$_2$, Mn, Fe[III], sulfate, CO$_2$)
Other additives	0	1 (e.g., surfactant)	1-2 (e.g., also macronutrients other than EA)
Environmental Chemistry	0	pH, Eh	pH, Eh potential and key redox pairs (e.g. Fe^{+3}/Fe^{+2}) Major cations (Na, K, Ca, Mg) and anions (PO$_4$, NO$_x$)
Microbes	0	1 (inoculation of contamination zone)	1+; controls on microbial transport not well understood
Key enzyme(s)	0	0	1-2; for cometabolism mechanisms
Microbial Processes			
Biomass	Constant (no growth)	Variable; linear growth;	Variable; multiple model options; multiple biomass indicators (e.g., enzyme activity)
Distribution	Dispersed	Dispersed	Dispersed, biofilm, and/or microcolony
Biofouling	neglect	Include simple algorithm	Include; needs research before practical
Mobility	neglect	neglect	Include when controlling processes better understood, e.g., chemotaxis
Substrate Kinetics	First-order	also dual-Monod	also minimum Monod

(Continued)

Table 7.4 (Concluded)

	Minimal	Adequate	Research
Microbial Processes (Continued)			
XAC Bioreaction Kinetics	First-order	also Monod, Haldane	also one or more of the Monod based schemes of Schmidt, Simkins, and Alexander (1985)
Coupling to Sorption	Sorbed substrate is unavailable	Simple desorption kinetics; sorbate is unavailable	Desorption kinetics by chemical and physical nonequilibrium processes
Coupling to Abiotic Reactions	Neglect; lump into combined decay rate	Simulate as independent, simultaneous processes	Competitive reaction kinetics, once environmental, media, and microbial controls on each are established
Miscellaneous Parameters			
Microbiology	Neglect; assume present, viable, & capable of transformation reactions	Site specific characterization of viability and reaction rates, preferably in situ	Identify key species and/or active enzyme systems in mineralizing consortia; model biomass as classes of consortium members

8   Abiotic Processes

Several abiotic reactions—photolysis, hydrolysis, nitro group reduction, polymerization, and covalent binding involving amino compounds—have been shown to affect explosives or other nitroaromatic compounds (Rosenblatt et al. 1989, Spanggord et al. 1980a, Leggett 1991, Wolfe and Macalady 1992, Ainsworth et al. 1991, Kaplan and Kaplan 1983). The significance of these reactions in the subsurface environment is reviewed in this chapter.

Photodegradation products formed in surface waters, and perhaps in very shallow soil waters, include phenolic-nitroaromatics. The amino and phenol compounds are potentially ionized under low pH conditions, which dramatically affect their transport behavior in porous media.

Explosives and explosive-associated compounds (XACs) are subject to both abiotic and microbially mediated reduction reactions, primarily involving the reduction of nitro groups to amino groups. The abiotic reduction occurs in aqueous solution and may be catalyzed at soil mineral surfaces. Considerable experimental evidence indicates that XACs are also subject to covalent bonding reactions (irreversible "sorption"). Neither the reducing agents (electron donors) nor the surface binding sites have not been identified unequivocally. Polymerization (a.k.a. conjugation or coupling) reactions to form azo and azoxy compounds have also been invoked to account for irreversible "sorption" of nitroaromatics.

8.1 Photolysis

Photolysis is the chemical alteration of a compound due to the direct or indirect effects of light energy. Direct photolysis requires only the input of light energy to proceed. Light energy absorbed by a molecule is reradiated as heat, fluorescence or phosphorescence, or if energy of the appropriate wavelength is sufficient (i.e., quantum), the molecular structure reorganizes irreversibly. Indirect or sensitized photolysis involves energy transfer from another photosensitized compound (e.g., peroxide or ozone) which reacts with the compound of interest. Humic compounds also appear to induce photolysis of nitroaromatics.

Photolysis is identified as one of the major processes affecting transformation of explosives in waste streams and surface water bodies (Spanggord et al. 1980a,b; Rosenblatt et al. 1989). Obviously, soil materials are essentially opaque to solar radiation (including UV wavelengths); thus photolysis is a potentially significant process only in the uppermost centimeters of soil and perhaps in plant tissues. Photolysis is relevant to groundwater transport questions primarily because it has potentially affected the XAC composition in wastewaters lagoons, which are common sources of subsurface contamination.

The two basic requirements for phototransformation are a light source of appropriate wavelength, λ, and intensity, I, to elevate the molecule to an excited state, and the phototransformation reaction from that excited state be competitive with deactivation processes such as quenching reactions (Harris 1990b).

Photolysis kinetics

Reaction kinetics in dilute solutions are typically first-order (or pseudo-first-order) for both direct and indirect photolysis (Mabey et al. 1983). The rate of transformation by direct photolysis may be described by:

$$\frac{dC}{dt} = -k_a \phi C \tag{8-1}$$

where k_a is a rate constant for light absorption [T^{-1}], and ϕ is the quantum yield of the reaction (moles reacted per Einsteins absorbed). An Einstein is a unit of light on a molar basis (Schnoor et al. 1987). The ϕ may be considered as the efficiency of the phototransformation. The photolysis rate is controlled by environmental conditions, such as the intensity and wavelengths of incident, solar insolation. The rate can be enhanced or impeded by the presence, respectively, of sensitizing or quenching compounds. Rates in natural waters may be 10-100 times greater than in distilled water, apparently due to the presence of sensitizing humic substances or nitrates (Hoigné et al. 1989).

Indirect or sensitized photolysis kinetics may be described by:

$$\frac{dC}{dt} = -k_2 X C = -k_p C \tag{8-2}$$

where k_2 is the rate constant for indirect photolysis, X is the concentration of the reaction intermediate, and k_p is the pseudo-first-order rate constant. As with any first-order reaction, the concentration at time t is:

$$C = C_o e^{-k_p t} \tag{8-3}$$

where

$$k_p = 2.3 \, \phi \, (\, \epsilon \, r \,) \, I_{o\lambda} \qquad\qquad (8\text{-}4)$$

and $I_{o\lambda}$ is the light intensity of wavelength λ [Einsteins·liter^{-1}·mol^{-1}], r is a correction factor for light attenuation with water depth, ϵ is the molar absorptivity [liters·cm^{-1}·mol^{-1}], and ϕ is the quantum yield, the fraction of absorbed light leading to a reaction (Harris 1990b, Schnoor et al. 1987). The light intensity at water depth z is $r I_{o\lambda}$, or $r I_\lambda = I_{o\lambda} \, e^{-K_e z}$.

Explosives photolysis

Phototransformation of TNT and associated nitroaromatics commonly involves oxidation of methyl groups, reduction of nitro groups, and dimer formation. These reactions generate nitrobenzenes (e.g., trinitrobenzene), benzaldehydes (Ar-COH), azoxydicarboxylic acids (e.g., Ar-(O)N=N-Ar'), and nitrophenols (Ar-OH) (Spanggord et al. 1980a, Mabey et al. 1983, Layton et al. 1987).

Heterocyclic XACs, e.g., RDX, HMX, also are susceptible to photolysis and form a variety of azoxy compounds. Dissolved humics do not appear to sensitize the photooxidation of HMX (Spanggord et al. 1982a). Transformation products tend to be of lower molecular mass than for the aromatic XACs, and include ammonia, formaldehyde, nitrate and nitrite, nitrous oxide, and N-nitroso-methylenediamine (Glover and Hoffsommer 1979).

Plants can take up dissolved XACs, but the environmental significance is probably minor (Pennington 1988). Certain plant species may bioconcentrate contaminants and thereby may serve as a medium for detecting low levels of soil contamination. The significance of photolysis within plant tissues is not known. Microcrystalline or adsorbed XACs in shallow soils or blowing dust conceivably could be susceptible to photolytic reactions; no data are available to elucidate this possibility.

8.2 Hydrolysis

Hydrolysis is a class of reactions in which a functional group, $-X$, in an organic compound $Ar\text{-}X$ reacts with water (as H_2O; H_3O^+, or OH^-) to form a new carbon-oxygen bond. The general form of these reactions is:

$$R\text{-}X + H_2O \xrightarrow{k_T} R\text{-}OH + X^- + H^+ \qquad\qquad (8\text{-}5)$$
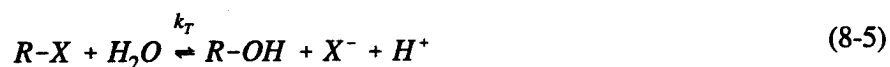
These reactions are distinct from completely acid-base (Section 8.3), hydration, addition, or elimination reactions that may also involve hydroxyl (OH^-) or hydronium (H_3O^+) ions. Common organic functional groups more susceptible to hydrolysis reactions include amines $(R\text{-}NH_2 \rightarrow R\text{-}OH)$, amides $(R\text{-}(C{=}O)\text{-}NH_2 \rightarrow R\text{-}(C{=}O)\text{-}OH)$, nitriles, and carboxylic acid esters. Functional groups that are generally resistant to hydrolysis include aromatic nitro compounds (e.g., TNT, DNT), aromatic amines (e.g., 2,4-diamino-6-nitrotoluene), aldehydes, heterocyclic polycyclic aromatic hydrocarbons, benzenes, and polycyclic aromatic hydrocarbons (Harris 1990b).

Photolysis and biotransformation can generate products similar to those from hydrolysis. Resolving the typically slow hydrolysis process from other reactions in the field is extremely difficult (Johnson, Palmer, and Fish 1989); thus most kinetics data are determined under controlled laboratory conditions. Experimental systems must be demonstrably abiotic and aphotic to increase the certainty regarding hydrolysis reactions. Adsorption also tends to impede hydrolysis (Mill and Mabey 1988) by removing the solute from aqueous solution.

Hydrolysis kinetics

A general rate expression for hydrolysis of neutral organic compounds in pure water (Mill and Mabey 1988) is:

$$\frac{dC}{dt} = -\left(k_a [H^+] + k_w + k_b [OH^-] \right) C \qquad (8\text{-}6)$$

where C is concentration of compound $R\text{-}X$, and k_a, k_w, and k_b represent the rate constants $[mol \cdot T^{-1}]$ for acid (H^+), neutral (water), and base (OH^-) hydrolysis, respectively; brackets indicate molar concentrations. Equation 8-6 neglects the potential contribution of other acids and bases to hydrolyze. The rate constants can be lumped into a total hydrolysis rate constant k_t as:

$$k_t = k_a [H^+] + k_w + k_b [OH^-] \qquad (8\text{-}7)$$

thus reducing Equation 8-6 to a simple pseudo-first-order expression:

$$\frac{dC}{dt} = -k_t [C] \qquad (8\text{-}8)$$

First-order rate expressions imply that the rate is independent of concentration and permits use of the half-life concept: $t_{1/2} = 0.693/k_t$. Values for k_t range between 10^{-1} and 10^{-7} day^{-1} and are functions of pH and temperature. Rates for XACs are typically small. Kinetics may be pseudo-first-order if a single type of hydrolysis dominates, but second- or higher-order is quite common

(Harris 1990a). A first-order kinetics model is adequate in most cases, at least as an initial approximation.

Reaction rate constants are inversely proportional to system temperature as may be described using the Arrhenius equation:

$$k = A\,e^{-[\,E_A/(RT)\,]} \tag{8-9}$$

where E_A is the Arrhenius activation energy [kcal·mol^{-1}], and A is a constant [T^{-1}]. Other theoretical (e.g., Eyring reaction rate) and empirical expressions are available to describe the temperature-dependence (Harris 1990b).

Hydrolysis of explosives

Most explosives and associated compounds are resistant to hydrolysis except at high pH's (>9), as are most nitroaromatic and aromatic amines (Harris 1990a, Spanggord et al. 1980a). A pH >9 is rare in freshwater environments.

Spanggord et al. (1980a, 1982b) report the alkaline hydrolysis kinetics of RDX as second-order in terms of (OH$^-$) and (RDX). Hydrolysis is very slow below 30 °C. Most reports indicate that the rate constant for HMX hydrolysis is typically two orders of magnitude smaller than RDX. Hoffsommer, Kubose, and Glover (1977) report the alkaline hydrolysis of RDX to yield nitrate, nitrogen, ammonia, nitrous oxide, formic acid, formaldehyde, and traces of H$_2$ in seawater (pH ~ 9).

The methylnitramine (H$_3$C-$\underline{N}$-NO$_2$) group of tetryl (see Table A.7 in Appendix A) undergoes slow hydrolysis to form picric acid (trinitrophenol) and methylnitramine, with a $t_{1/2}$ of 302±76 days at 20 °C and pH 6.8 (Kayser, Burlinson, and Rosenblatt 1984, Rosenblatt et al. 1989, Layton et al. 1987). Tetryl is one of the few explosives that undergo hydrolysis under environmental conditions (15-25 °C and circumneutral pH).

8.3 Acid-Base Dissociation Reactions

Acid–base dissociation reactions involve the reversible loss or addition of a proton or an electron, by the Brønsted-Lowery convention adopted here. A Brønsted acid donates a proton (H$^+$) and the base accepts or receives the proton (Stumm and Morgan 1981). Strong, inorganic acids such as hydrochloric (H$^+$Cl$^-$) and sulfuric ([H$^+$]$_2$[SO$_4$$^{-2}$]) tend to be completely dissociated at environmental pH's. Weak, organic acids, such as acetic acid (see Figure 8.1 and Table 8.1), tend to be only partially dissociated.

Amino compounds are very weak organic bases. The dissociation of a weak organic base may be expressed as the dissociation of its conjugate acid.

Figure 8.1. Relative distribution of dissociation constants (pK$_a$s) for a variety of nitro- and amino-aromatic compounds

For example, the dissociation reaction for amino-benzene (aniline) may be written as the dissociation of the anilinium ion:

$$Ar\text{-}NH_3^+ \quad + \quad H_2O \quad \rightleftharpoons \quad Ar\text{-}NH_2^o \quad + \quad H_3O^+ \qquad (8\text{-}10)$$

where the Ar represents the aromatic ring structure. Equation 8-10 indicates that high pH (lower [H$_3$O$^+$] on the right side of the equation) favors the forward, dissociation reaction, while low pH (higher [H$_3$O$^+$] favors the reverse reaction (Le Châtelier's principle). The undissociated amino compound dominates at higher pHs.

The acid dissociation constant, K_a, is defined as the equilibrium ratio of product activities to reactant activities. For Equation 8-10, the K_a may be defined as:

Table 8.1
Dissociation Constants (pKa's) for Ionizable Explosive-Associated Compounds (XACs), Homologs, and Similar Compounds

Compound[1] [as Brønsted Acid (proton donor)]		pKa	Reference[2]
Amines: $R\text{-}NH_3^+ \leftrightarrow R\text{-}NH_2^0$		~10	Harris and
Ammonium: $NH_4^+ \leftrightarrow NH_3^0$		9.3	Hayes (1990)

Aminobenzene Series:[3] $C_6H_{(6\text{-}x\text{-}y\text{-}z)}(NH^-)_x(NH_2^0)_y(NH_3^+)_z^{[z\text{-}x]}$

Aminobenzene (Aniline), AB°	$y=1 \leftrightarrow x=1$	27	Harris and Hayes (1990)
Anilinium (AB⁺)	$z=1 \leftrightarrow y=1$	4.603	Harris and Hayes (1990)
1*,3-diaminobenzene (1,3DA-B)	$x=1, y=1$	~5.0	Hammett
1*,4-diaminobenzene (1,4DA-B)	$\leftrightarrow x=2$	~6.4	Hammett
1*,3,5-triaminobenzene (1,3,5TA-B)	$x=2, y=1$ $\leftrightarrow x=3$	~5.5	Hammett

Nitro-Aminobenzene Series: $C_6H_{(6\text{-}b\text{-}x\text{-}y\text{-}z)}(NO_2^0)_b$ $(NH^-)_x(NH_2^0)_y(NH_3^+)_z^{[z\text{-}x]}$

2-Amino-Nitrobenzene (2A-NB)	$b=1, z=1$	−0.28	Dean (1985)
3-Nitro-Aminobenzene (3A-NB)	$\leftrightarrow b=1, y=1$	2.46	"
4-Nitro-Aminobenzene (4A-NB)		1.01	"
2-Amino-1,3-Dinitrobenzene		−5.23	Dean (1985)
(2A*-13DNB)	$b=2, z=1$		
4A*-13DNB	$\leftrightarrow b=2, y=1$	−4.25	"
5A*-13DNB		0.229	"
2*,4,6-Trinitro-Aminobenzene	$b=3, z=1$	−10.23	Dean (1985)
(2A-1,3,5TNB)	$\leftrightarrow b=2, z=2$		Dean (1985)

Aminotoluenes (Toluidines):
$C_6H_{(6\text{-}a\text{-}b\text{-}c\text{-}x\text{-}y\text{-}z)}$ $(CH_2^-)_a$ $(CH_3^0)_b$ $(CH_4^+)_c$ $(NH^-)_x$ $(NH_2^0)_y$ $(NH_3^+)_z^{(c+z)\text{-}(a+x)}$

Toluene	$b=1 \leftrightarrow a=1$	35	Harris and Hayes (1990)
2*-Aminotoluene (2A-T)	$b=1 \leftrightarrow b=1$	4.450	Dean (1985)
3*-Aminotoluene (3A-T)	$z=1 \quad y=1$	4.710	"
4*-Aminotoluene (4A-T)		5.080	"
2*5-Diaminotoluene (25DA-T)	$b=y=z=1$	~6.6	Hammett
3*5-Diaminotoluene (35DA-T)	$\leftrightarrow b=y=z=1$	~5.2	"
2,3,5*-Triaminotoluene (235TA-T)	$b=z=1, y=2$	~7.0	Hammett
2,4*,6-Triaminotoluene (246TA-T)	$\leftrightarrow b=1, y=3$	~5.6	"

			(Continued)

[1] The "*" indicates the proton-donating group.
[2] "Hammett" refers to estimation by the Hammett method (Harris and Hayes 1990); LFER = linear free energy relation.
[3] Functional group counter variables (a,b,x,y) indicate stoichiometry of reactants (left of double arrow) and products (right side) for the general group formula; variables are zero unless otherwise specified.

Figure 8.1 (Concluded)

Compound [as Brønsted Acid (proton donor)]		pKa	Reference
Amino-Nitrotoluene Series: $C_6H_{(5-b-c-y-z)}$ $(CH_3^o)(NO_2^o)_b$ $(NH_2^o)_y$ $(NH_3^+)_z^{(c+z)-(a+x)}$			
4*-Amino-2-Nitrotoluene (4A-2NT)	$b=1, z=1$ ↔ $b=1, y=1$	~3.2	Hammett
2*,4*-Diamino-6-Nitrotoluene, 2,4*-Diamino-6-Nitrotoluene (24DA-6NT)	$b=1, z=2$ ↔ $b=1,$ $y=z=1$ ↔ $b=1, y=2$	~1.5, ~3.6	Hammett
4-Amino-2,6-Dinitrotoluene (4A*-46DNT)	$b=2, z=1$ ↔ $b=2, y=1$	~1.2	Hammett
2-Amino-4,6-Dinitrotoluene (2A*-46DNT)	$b=2, z=1$ ↔ $b=2, y=1$	~0.6	Hammett/ LFER
Phenols, Ar-OH: $C_6H_{(6-i-j-k-b-y-z)}(O^-)_i(OH^o)_j(OH_2^+)_k(NO_2)_b$ $(NH_2)_y$ $(NH_3^+)_z^{[k+z-i]}$			
Phenol (POH)	$j=1$ ↔ $i=1$	9.99	Dean (1985)
2-Nitro-Phenol (2-NP)		7.22	Dean (1985)
3-Nitro-Phenol (3-NP)	$j=1, b=1$	8.36	
4-Nitro-Phenol (4-NP)	↔ $i=1, b=1$	7.15	
2,4-Dinitro-Phenol (2,4-DNP)	$j=1, b=2$	4.08	Dean (1985)
2,6-Dinitro-Phenol (2,6-DNP)	↔ $i=1, b=2$	3.713	
2,4,6-Trinitro-Phenol (2,4,6-TNP, Picric Acid)	$j=1, b=3$ ↔ $i=1, b=3$	0.419	Dean (1985)
2-Amino-Phenol pK_1-amine:	$j=1, z=1$ ↔	9.28,	Dean (1985)
3-Amino-Phenol pK_2-phenol:	$j=1, y=1$	9.72	
4-Amino-Phenol CHECK these		9.38,	
	$j=1, y=1$ ↔	9.87	
	$i=1, y=1$	8.50, 10.3	
1-Aminonaphthalene $Ar-NH_3^+$ ↔ $Ar-NH_2^o$		3.94	Szecsody, Striele, and Pavolka (1993)
Water H_2O ↔ OH^-		14.0	Stumm and Morgan (1981)
Hydronium H_3O^+ ↔ H_2O		0.0	
Carboxylic Acid $H_2CO_2^o$ ↔ HCO_2^- ↔ $CO_2^=$		6.36, 10.33	Dean (1985)
Acetic Acid CH_3COOH^o ↔ CH_3COO^-		4.756	Dean (1985)
Nitric Acid HNO_3 ↔ NO_3^-		−1.38	
Sulfuric Acid H_2SO_4 ↔ HSO_4^- ↔ $SO_4^=$		~ −3.0, 1.99	Dean (1985)
Hydrochloric Acid HCl ↔ $H^+ + Cl^-$		−6.1	

$$K_a = \frac{a_{H_3O^+} \, [Ar\text{-}NH_2^o]}{[Ar\text{-}NH_3^+]} = 10^{-4.603} \qquad (8\text{-}11)$$

where the brackets indicate molar concentration [mol·L⁻¹], and the assumptions made are that the activity of water is unity, and that the activity coefficients for the aromatic compounds are approximately 1.0 (i.e., an ideal solution). These approximations are generally good at solute concentrations less than 0.01 M (Harris and Hayes 1990). Taking the negative $\log_{10}$ of Equation 8-11 and substituting of the definitions of pH and pK_a [p(x) = −log (x)] yields:

$$pH - pK_a = \log \frac{[Ar\text{-}NH_2^o]}{[Ar\text{-}NH_3^+]} \qquad (8\text{-}12)$$

Ionized and unionized concentrations are equal when pH equals the pK_a. At pHs above the pK_a the neutral species dominates (e.g., aniline), while at pHs below the pK_a the ionic species dominates (e.g., anilinium). Dissociation of typically low concentrations of weak organic acids in the environment is usually controlled by other acid-base dissociation reactions (e.g., bicarbonate-carbonate, water).

Environmental pHs typically range between 5 and 8. Thus, an acid may be significantly dissociated (>1 percent) if its pK_a falls between 3 and 10 (these ranges are delineated in Figure 8.1). An organic acid (or conjugate base) with a $pK_a \leq 4$ is completely (>99 percent) dissociated at pHs > 6. For organic base reactions written as the dissociation of the conjugate acid (as for aniline), the uncharged species represents the dissociated form. For acids, the uncharged species represents the undissociated (protonated) state the concentration of which would appear in the denominator of Equations 8-11 and 8-12.

Most of the XACs that are susceptible to acid-base dissociation are weak bases due to the presence of amino functional groups produced in biotic or abiotic reduction reactions (see Sections 8.4 and 7.7). Phenolic XACs (e.g., photolytic reaction products) tend to be weak acids with high pK_as. Nitro and methyl groups are not susceptible to dissociation reactions at environmental pHs.

Whether a solute is ionized or not can dramatically affect its environmental behavior. An uncharged organic base or acid may sorb weakly by hydrophobic partitioning or perhaps by specific interactions with soil solid functional groups. Organic cations (e.g., $Ar\text{-}NH_3^+$) may sorb to cation exchange sites, while the anionic forms (e.g., $COOH^-$ or $Ar\text{-}NO^-$) may sorb very little. A cationic amino-aromatic species (e.g., anilinium) is less susceptible to

coupling reactions to form azo compounds than the uncharged species would be (Morrison and Boyd 1983).

The pK_a data for ionizable XACs are sparse. Most of the amino XACs have conjugate acids with very low pK_as and are largely uncharged at common environmental pHs. One can estimate unknown pK_as by comparing the XAC molecular structure against the structures of similar compounds for which pK_as are known and for which statistical correlations have been presented (Harris and Hayes 1990). The other compounds may be part of a homologous series (e.g., toluene, nitrotoluene, aniline, etc.) or compounds with electron-drawing groups similar to nitro groups common in XACs. Many of the pK_as presented in Table 8.1 utilize the Hammett relations established for a limited group of compounds (see Harris and Hayes (1990) for a discussion).

8.4 Abiotic Reduction Reactions

Oxidation-reduction (redox) reactions are those involving the transfer of electron(s) between reactants. Redox reactions may be described in terms of two half-reactions—the oxidation half-reaction donates the electron(s), the reduction half-reaction accepts the electron(s). One of the challenges in environmental redox chemistry is to establish which of the multitude of competing half-reactions are involved in the reaction of interest. For example, the electron donor involved in the nitro-to-amino reduction reaction in explosives is not known with certainty. The sequential reduction of explosive nitro groups $(Ar-N[+III]O_2^\circ)$ to form amino compounds $(Ar-N[-III]H_2^\circ)$ involves a series of reactions similar to:

$$\langle\!\bigcirc\!\rangle\!-C-N{\overset{\nearrow O}{\underset{\searrow O}{}}} + 6\ H_3O^+ + 6\ e^- \rightleftharpoons \langle\!\bigcirc\!\rangle\!-C-N{\overset{\nearrow H}{\underset{\searrow H}{}}} + 8\ H_2O$$

$$(8\text{-}13)$$

Nitroso $(Ar-N[+I]O)$, hydroxylamine $(Ar-N[-I]HOH)$, and other possible reaction intermediates (Wolfe and Macalady 1992) are not shown in Equation 8-13. Each nitro-to-amino half-reaction involves the transfer of six electrons to the nitrogen. The presence of six hydronium ions in Equation 8-13 would suggest an acidity dependence of the reaction rate constant. However, the influence of pH is uncertain since the reaction diagram does not show other steps in the reaction mechanism that may be rate limiting (Wolfe and Macalady 1992).

One of the greatest obstacles to the general understanding and modeling of the abiotic reduction reactions is the uncertainty regarding the source of the electrons in Equation 8-13, i.e., the reductant in the reaction. Nitro-to-amino

reduction reactions have been observed in many compounds in both natural and synthetic systems (Theng 1974, Wolfe and Macalady 1992). However, the precise identity of the electron donor(s), as well as many reaction products and intermediates, has eluded most investigators, particularly in natural systems (Macalady, Tratnyek, and Grundel 1986, Wolfe 1992, Schwarzenbach et al. 1990). This frustrating situation is not surprising in light of the complexity of multiple and coupled reactions in heterogeneous, natural systems. Difficulty in analytical characterization of reactants and products further exacerbates the problem.

The most commonly invoked reducing agents in natural systems, mostly by inference, are based on the ferrous-ferric iron redox pair ($Fe^{2+} \leftrightarrow Fe^{3+} + e^-$). Iron is a common redox-sensitive metal that occurs in aqueous solution (the reduced, ferrous form being more soluble), as oxyhydroxide solids (e.g., $Fe[+III]OOH$), and in an organometallic compound such as hematin, or iron porphyrin (Weber and Wolfe 1987, Schwarzenbach et al. 1990, Gantzer and Wackett 1991, Pennington and Patrick 1990).

Redox reactions involve two half-reactions, which may be described with second-order rate laws. If the reductant concentration is fairly constant (an excess or stable supply) the reaction can be described using a pseudo-first-order rate law. Indeed, most abiotic reduction kinetic studies proceed from an assumption of first-order kinetics from Macalady, Tratnyek, and Grundel (1986):

$$\frac{d C_{xac}}{d t} = - k_{obs} [C_{xac}] \qquad (8\text{-}14)$$

where the k_{obs} pseudo-first-order, rate constant [T^{-1}] is a function of reductant concentration and oxidation rate:

$$k_{obs} = k_{red} [C_{red}] \qquad (8\text{-}15)$$

where k_{red} is the second-order rate constant [$M^{-1} \cdot T^{-1}$] for the reduction reaction.

Oxidation-reduction reactions rates are highly variable but are typically slow relative to simple adsorption reactions, for example. Natural systems with multiple redox couples are quite likely to not be at equilibrium, even for high residence-time groundwater systems (Scott and Morgan 1990, Lindberg and Runnells 1984). Microbial processes are able to accelerate some reduction reactions.

The abiotic, nitro-to-amino reaction is sensitive to Eh variation, but the dependence of reduction rates on redox potential is not established (Macalady, Tratnyek, and Grundel 1986). Redox potential does not appear to affect the

rate of abiotic reduction, at least for certain nitrogen, azoaromatics compounds, e.g., azobenzene (Weber and Wolfe 1987).

Nitro reduction reactions have been reported to occur in aqueous solution. In other cases, the reduction appears to require or is accelerated by a solid substrates (heterogeneous catalysis). Interactions between the reactants and the surface act to lower the activation energy (kinetic barrier) to reaction. Clay minerals and other soil materials such as metal oxyhydroxides or soil organic macromolecules (e.g., humic or fulvic compounds) particulates have been suggested as substrates for catalyzing abiotic organic reactions (Theng 1974).

Reduction reactions in the aqueous phase

The nitro-to-amino reduction has been observed to proceed abiotically in homogeneous aqueous solution. Schwarzenbach et al. (1990) and Dunnivant, Schwarzenbach, and Macalady (1992) report the reduction of several substituted nitrobenzenes and nitrophenols mediated by small amounts of iron porphyrin or hydroquinone moieties under anaerobic conditions in the aqueous solutions of reduced sulfide. Other iron-bearing enzymes or solutes may also affect such a reduction. The hydroquinone and other moieties occur in dissolved natural organic matter. Schwarzenbach et al. (1990) describe a popular conceptual model in which the organometallic or quinone compound acts as an electron carrier between a more reducing environment (their sulfide solution) and the nitro-compound:

$$(Ar\text{-}NO_2)_{ox} \qquad (Electron\ Carrier)_{ox} \qquad (Bulk)_{ox}$$

$$+ n\ e^- \qquad - n\ e^- \qquad + n\ e^- \qquad - n\ e^-$$

$$(Ar\text{-}NH_2)_{red} \qquad (Electron\ Carrier)_{red} \qquad (Bulk)_{red}$$

Schwarzenbach et al. (1990) also observe that the rate of nitro reduction is strongly dependent on pH, particularly as the system pH nears the pK_a of the reductant or contaminant. In natural systems, these organometallic and hydroquinones may arise from (micro) biological activity. Clearly, these mechanisms involve organic solutes and electron-transfer mechanisms that may also be active in microbes, but are generally considered abiotic reactions because microbes are not directly involved.

Spanggord et al. (1982b) evaluated several organic reductants (hematin or ferriprotoporphyrin, ferrous iron, sodium dithionate, bisulfide) for effects on HMX. The only significant reactions observed were for dithionite ($S_2O_4^{2-}$) at a pH of 11.2 for which only 30 percent reduction was attained.

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Surface catalyzed reduction

Considerable evidence suggests that some abiotic reduction reactions require activation by solid catalysts, e.g., iron compounds, clay minerals, or organic macromolecules. Whether these surfaces simply catalyze a reaction between adsorbates or act as the electron donor is probably system specific.

Weber and Wolfe (1987) and Wolfe (1992) examined the abiotic reduction of aromatic azo compounds (e.g., azobenzene: $Ar-N=N-Ar+4H^+ +4e^- \rightarrow 2$ aniline). They propose a multicomponent working model to describe the surface-catalyzed reaction:

$$P:R \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} P + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P:S \tag{8-16}$$

$$\downarrow k_r \qquad\qquad \downarrow k_w \qquad\qquad \downarrow k_s \quad .$$

where $P:R$ represents the compound bound at reactive, adsorbent sites, $P:S$ represents the compound in a nonreactive adsorbate reservior, P is the pollutant solute, and S is the sediment which includes both reactive and nonreactive sites. The k_1 and k_{-1} rate constants describe the solute partitioning to the nonreactive sediment compartment; at equilibrium these are described by the distribution coefficient K_d. The k_2 and k_{-2} rate constants describe the solute partitioning to the reactive sites. The k_1 and k_2 are second-order rate constants, depending on both solute and sorbate concentrations; the reverse rate constants are first-order. The transformation (or "disappearance") rate constants, k_r, k_w, and k_s, describe the first-order reaction kinetics for the pollutant in the reactive site, water, and nonreactive sorbate compartments, respectively. The Weber-Wolfe model is consistent with their experimental observations:

a. Reaction rates are negligible in the aqueous phase alone, i.e. sediment surfaces are required.

b. Reaction rate constants tend to decrease with increasing hydrophobicity of the contaminants, i.e., increased partitioning to the nonreactive P:S compartment impedes reactions.

c. Reaction rate constants are dependent on sediment concentration.

They do not identify the specific reaction sites responsible for the observed reduction. However, heat sterilization (three-, 20-min, autoclave treatments at 120 °C and 60 psi (414 kN/m²) within 48 hr) increased the half-life by more than an order of magnitude (x11.8), indicating that the unknown reactant is heat-labile. They could identify no correlation between reaction rate and reduction potential.

Diffusion of reactants and products to and from the reactive sites (R:) must be included to adequately model the role of solids in these systems (Wolfe

1992). Weber and Wolfe (1987) develop a pseudo-first-order rate expression (k_{obs}) for the model described by Equation 8-16:

$$k_{obs} = \frac{k_2 [S]}{1 + K_d [S]} \qquad (8\text{-}17)$$

with the following assumptions: (a) no reactions occur in the P:S compartment, i.e., $k_s \approx 0$; (b) equilibrium is established quickly for the nonreactive compartment relative to the reactive sites, i.e., $k_1 \gg k_2$; and (c) diffusion to reactive sites is the rate-limiting mechanism, i.e., $k_r \gg k_2$, k_w, and k_s. Wolfe (1992) suggests that an alternative model, indistinguishable with the available experiment data, would be the steady-state diffusion of the unidentified soil reducing agent(s) into the aqueous phase at low concentrations. The Weber-Wolfe model reactive sites are strictly sites of heterogeneous catalysis with no mechanism for poisoning or otherwise limiting their reductive capacity.

Assessing the redox potential of subsurface media

Aqueous redox reactions tend to be fairly slow and nonequilibrium systems may be the rule rather than the exception, even in high residence-time groundwater systems (Lindberg and Runnells 1984). This rule is particularly likely where biotic and/or abiotic reactions are active (Scott and Morgan 1990).

The most common measurement of the redox condition of an aqueous system is redox potential, Eh, measured relative to a standard hydrogen electrode. Such redox intensity measurements are valid only if electrochemically active constituents are present in detectable amounts and all redox couples are at equilibrium. Eh correlates poorly with the redox reaction rates or the system's capacity to reduce compounds. Eh is only a reflection of key processes that may affect abiotic reduction, including chemical solubility, speciation, and activity (Scott and Morgan 1990).

Redox intensity measures of the aqueous phase, measured as Eh or concentration ratios of redox pairs do not provide a very reliable indicator of the redox capacity of the porous medium. Redox capacity of a groundwater system includes not only aqueous species but also mineral, gas, and microbial components (Scott and Morgan 1990). Much if not most of the redox capacity lies in the solids (Barcelona and Holm 1991), which have tremendous implications not only for attempts to model redox reactions (including microbial processes) but also for in situ remediation technologies that rely on injection of oxidants, reductants, or nutrients.

Scott and Morgan (1990) suggest that a form of redox titration be conducted to assess the oxidation (OXC) or reduction (RDC) capacity of a system:

$$OXC = \sum n_i \, [OX]_i - \sum n_i \, [Red]_i = - RDC \qquad (8\text{-}18)$$

where [OX] and [Red] are molar concentrations of the oxidants and reductants, respectively, with n_i equivalents. This equation is essentially a chemical oxidation demand evaluation of the medium. The relevance of a reduction capacity determined with a strong oxidizing agent such as hydrogen peroxide is uncertain. A titrant that would measure a soils capacity to reduce explosives would have to be identified. If the reduction of TNT, for example, in natural soils is predominantly abiotic, it appears that soils have a finite capacity for affecting the reduction, as indicated by the persistence of TNT in solution at contaminated sites.

Explosives reduction

There has been sufficient research on substituted (halogen, aryl, or nitro) anilines to suggest an abiotic nitro reduction mechanism. Much less experimental data are available on explosives per se. Abiotic reactions are implicated in several experiments in which explosives or associated compounds are contacted with soil material (e.g., Pennington and Patrick 1990). Column breakthrough experiments by WES personnel indicate that an abiotic process may be inducing TNT reduction to amino compounds and strongly retarding and/or binding TNT or its reaction products. Yet, N-heterocyclic explosives (RDX, HMX) pass through the column with minimal retardation and reduction.

The observation of rapid reactions and strong retardation of TNT in packed columns of previously uncontaminated soils appears to be in conflict with some field observations of extensive groundwater plumes of TNT (e.g., at CAAP; see Chapter 2). Though it is difficult to generalize in the absence of abundant data, speculations may be offered. The disparate behavior between soils and aquifers may indicate that the strong retardation process(es) observed in some soils are less active in aquifers. This decrease in activity may arise from the absence of abundant organic matter in sandy aquifer systems or may be related to anaerobic microenvironments that can develop in organic soils, but are less common in shallow groundwaters. The disparate behavior of TNT in certain soils may reflect the intensity of loading relative to the systems' reductive capacity.

The limited data on N–heterocyclic ring explosives (e.g., RDX, HMX) indicate that these compounds are much less susceptible to abiotic reduction. This lack of reactivity suggests that the reaction mechanism affecting nitro-aromatic XACs (e.g., TNT, DNT, TNB) is inoperative with heterocyclics. The most obvious structural differences between TNT and RDX, for example, are: (a) the TNT has aromatic π-electrons; (b) TNT has a methyl group; and (c) the RDX nitro groups are attached at the heterocyclic nitrogens, whereas all TNT nitros are bound to ring carbons. These structural features clearly exert some influence o the reactivity of the compounds. Perhaps the aromatic

π-electrons are responsible for a nucleophile donor-acceptor reaction at reactive sorption sites; the absence of the π-electrons in RDX may be sufficient to reduce binding.

Some XAC adsorption behavior appears to be influenced by redox conditions. For example, TNT, 2-amino-4, 6-dinitrotoluene, and 4-A-2, 6-DNT sorption is slightly greater (higher K_d) under reducing conditions (Eh = -150 mV) than under oxidizing conditions (+450 mV) (Pennington and Patrick 1990). The reason for the effect is undetermined but likely is related to the redox-sensitivity of the unknown reductant (electron donor) compound or competing adsorbates. Perhaps the reductant or catalyst surface is only stable (accessible) under oxic or suboxic conditions.

Resolution of abiotic and biotic reduction

It is extremely difficult to resolve unequivocally abiotic from microbially mediated reduction reactions. The reduced XAC products appear to be indistinguishable. Neither of these competing or coupled reaction pathways is sufficiently well established. The redox state in the environment is driven primarily by microbial processes; thus resolving abiotic from biotic reactions is an artificial exercise, but necessary to develop a better appreciation of both biotic and abiotic processes.

Experiments can be designed to accentuate either biotic or abiotic reactions, but it is very difficult to completely preclude one or the other with certainty. The most common approach is to impede the microbial processes by either chemical (e.g., Hg salts), thermal (e.g., autoclave), or irradiative (e.g., γ-radiation) means. Still the influence of biochemical remains (e.g., exudates, lysed cell matter) retains some level of uncertainty. The possibility that these antimicrobial methods impact the abiotic process must be addressed, perhaps with parallel experiments (treated and untreated) in synthetic and sterile mixtures of suspected solid reductants.

Trends in column breakthrough experiments may provide some indication as to a dominant mechanism (Townsend, Myers, and Adrian 1995). If a soil shows an finite, exhaustible capacity to reduce or attenuate TNT, then an abiotic mechanism is indicated. Attenuation rates that are independent of temperature would also suggest an abiotic mechanism, assuming that microbial processes are much more temperature sensitive. Attaining a reduced, steady-state, effluent concentration would be inconclusive by itself since either mechanism could generate such an observation.

8.5 Irreversible Surface Reactions

Evidence for strong binding of nitroaromatics, including some XACs, on soil/aquifer solids is accumulating (Szecsody, Streile, and Pavalko 1993,

Wolfe 1992). Aniline compounds, for example, tend to bind relatively quickly and irreversibly to soil components (Bollag, Minard, and Liu 1983; Hsu and Bartha 1974). Sorption experiments with TNT commonly show a loss of mass, presumably to a irreversible sorption or binding process.

The surface-catalyzed reactions described previously yield products that are necessarily proximal to solid surface. Reaction mechanisms to account for the apparently irreversible binding of XACs to soil solids have been proposed for many aromatic and nitroaromatic compounds, as follows:

a. Covalent bonding to specific functional groups in soil organic and/or mineral solids.

b. Polymerization and oligomerization of XACs and soil organics.

c. Entrapment within clay mineral interlamellae or other nanoporous material (e.g., zeolites).

Reactions have been identified or are implicated between amino- or nitro-aromatics and humic substances (Parris 1980), clay minerals (Ainsworth et al. 1991, Szecsody, Streile, and Pavalko 1993, Leggett 1990), or unidentified soil components (Hsu and Bartha 1974, Macalady, Tratnyek, and Grundel 1986).

Covalent binding to soil humics

Parris (1980) hypothesizes that the sorption of aromatic amines $(Ar–NH_2)$ to humic carbonyls—aldehyde $(R_{Hum}–CH=O)$ or ketone $(R_{Hum}–[C=O]–R'_{Hum})$ moieties—proceeds by the initial, rapid, and reversible formation of an imine $(R_{Hum}–C=N–Ar)$:

$$Ar–NH_2 + O=C–R \rightleftharpoons Ar–N=C–R + H_2O \qquad (8\text{-}19)$$

$$\text{amine} \qquad \text{carbonyl} \qquad \text{imine}$$

This reaction is followed by a series of very slow and not readily reversible reactions by which the aromatic amine is covalently bound to the humic structure. The proposed slow reaction is addition of the amine to a quinoidal structure $(O=Ar=O)$, oxidation to form a nitrogen--substituted quinoid ring, and finally a possible internal reaction locking the N into a heterocyclic humate structure. The covalently bound amine would be very resistant to extraction or reaction (e.g., acid or base hydrolysis). The reaction mechanism is not substantiated experimentally, but is consistent with observations. Layton et al. (1987) report that the loss of substituted anilines may be due to binding to carboxyl groups in soil humic acids, proteins, or lipids.

The rate of binding of aniline varies as the product of aniline and humate (first-order in each), but the problem is probably not a simple second-order

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reaction (Parris 1980) because multiple reaction sites (S_i) are likely to be involved. The rate expression for aniline concentration ($[A]$) is:

$$\frac{d[A]}{dt} = -\sum_i k_1 [A][S_i] \qquad (8\text{-}20)$$

where k_1 is the rate constant for the reaction site S_i. At time t = 0, the $[S_i]_o = C_i[Hum]_o$ where C_i is a constant for each class of humate, and Equation 8-20 may be expressed as:

$$\frac{d[A]}{dt} = -\left(\sum_i k_i C_i\right)[A]_o[Hum]_o \qquad (8\text{-}21)$$

The term within the parentheses is an apparent second-order rate constant estimated by the initial rate of [A] disappearance over the initial concentration product $[A]_o[Hum]_o$, i.e., solving Equation 8-21 for the apparent second-order rate constant. Parris (1980) also reports steric inhibition of the sorption by ortho substituents regardless of their electronic effects (e⁻ withdrawing -Cl or -NO$_2$ or donating -CH$_3$).

Bollag, Minard, and Liu (1983) presented evidence that several chloro- and diethyl-substituted aniline compounds bonded with the phenolic (R-OH) functional groups of soil humus. Cross-linking between substituted anilines and carboxyphenols appears to be initiated by extracellular laccase enzymes from the fungus *Rhizoctonia praticola*. Hybrid dimers, trimers, and tetramers (oligomers and polymers) reaction products were identified, thus indicating binding of aniline to quinones by cross-linking between the N and an aromatic ring carbon to form a imine (anil). Products of such cross-coupling would be incorporated quickly into the soil organic matter matrix and become very difficult to extract (Bollag, Minard, and Liu 1983).

Hsu and Bartha (1974) found that 3.4-dichloroaniline (DCA) chemically binds to soil humics by at least two mechanisms, based on the recovery of ^{14}C-labeled DCA. Approximately one-half of the 3,4-DCA was released by base hydrolysis; the remainder was recovered only by combustion. The relatively weakly bound, hydrolyzable portion of DCA is attributed to carbonyl groups to form imine or anilinoquinone forms (x-linking). The nonhydrolyzable portion is attributed to incorporation into heterocyclic rings or forming ether bonds.

Weber, McGinley, and Katz (1992) report evidence of covalent binding of aromatic amines to the carbonyl moieties in natural organic matter using direct spectroscopic evidence (^{15}N-nuclear magnetic resonance). Observations were interpreted as supporting a nucleophilic addition mechanism. Their goal is to enhance covalent binding as a contaminant immobilization technique.

Polymerization/conjugation/coupling

The ability of clay minerals to catalyze (activate or inhibit) polymerization of aromatic compounds has been recognized for many years (Theng 1974). Szecsody, Streile, and Pavalko (1993) and Ainsworth et al. (1991) report a surface-catalyzed reaction of 1-aminonaphthalene (A^+) on smectite clay (X). They propose a two-step mechanism:

$$X^{[-]} Na^{[+]} + A^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X^{[-]} A^{[+]} + Na^+$$

$$XA + A^+ \overset{k_2}{\rightarrow} XAA + 2H^+$$

(8-22)

in which the ionized form A^+ $(C_{10}H_8NH_3^+;$ $pK_a=3.93)$ is adsorbed fairly quickly (hours) in a cation-exchange reaction, and then a surface-catalyzed reaction polymerizes the aminonaphthalene to 4-ring dimer complexes, N-(4-aminonaphthyl)-1-naphthylamine (AA) which sorbs strongly to the mineral surface (X). The kinetic expressions for each component of the reaction (Equation 8-22) may be described by:

$$\frac{d[A]}{dt} = k_{-1}[XA] - k_1[A][X] - k_2[XA][A] \quad (a)$$

$$\frac{d[X]}{dt} = k_{-1}[XA] - k_1[A][X] \quad (b)$$

$$\frac{d[XA]}{dt} = -k_{-1}[XA] + k_1[A][X] - k_2[XA][A] \quad (c)$$

$$\frac{d[XAA]}{dt} = k_2[XA][A] \quad (d)$$
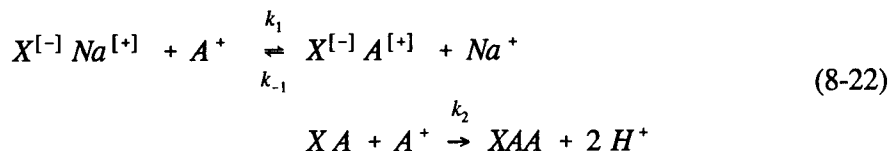
(8-23)

The charge signs are omitted for clarity. The reaction is rapid in batch experiments—98 percent conversion in a 24-hr batch test with excess sites (low solute concentration)—but is expected to be much lower under field conditions. If sites are not in excess, i.e., site-limited, reaction rate may be slower. Polymerization products may be very difficult to extract. This reaction mechanism could be tested by conducting experiment(s) with unionized amino-compounds, i.e., at pHs above their pK_a (see Section 7.4), or including solutes that would impede XAC sorption (competitive sorbates or site poisoning).

8.6 Summary and Research Recommendations

Photolysis and hydrolysis are relatively minor processes for XACs in the subsurface, though photolysis is a major transformation process in photic surface waters. Some of the transformation products of photolysis and abiotic or biotic reactions are ionizable, which introduces a significant complication to the modeling of XAC transport—a pH and probably an Eh influence on XAC

speciation and resulting behavior as an adsorbate and reactant. Aqueous complexation of XACs with other solutes (including other XACs) is possible but poorly understood.

The role of mineral and soil organic surfaces in catalyzing the reduction of XAC solutes or binding the XACs is clearly very important, though the precise mechanism is undetermined. That these catalyzed reactions seem to be more significant in soils than in aquifers suggests that catalyst and/or reductant is a soil component that is scarce in the deeper subsurface. This hypothesis would be consistent with the proposed electron-transfer mechanism via dissolved natural organic matter (e.g., iron porphyrins), which likely would be at higher concentrations in soils than in sandy aquifers. Anaerobic microenvironments are common in organic-rich soils, which would provide a reduction zone for electron carriers proximal to unreduced nitro compounds.

The phenomenon of XAC surface binding and incorporation into soil organic macromolecules is yet to be substantiated, though there is strong evidence for other amino-aromatics. Likewise, the possible polymerization or oligomerization of XACs and soil organics is intriguing but unconfirmed for XACs.

Proposed conceptual model

The conceptual model of Weber and Wolfe (1987) could be expanded to include additional reactive sites and mechanisms (see Figure 8.2). Irreversible binding and surface polymerization pathways are required. The concept of reduction capacity for a soil or aquifer material could be addressed by introducing a "reductant reservoir" which either contains a finite and exhaustible supply of reductant or re-reduces electron carrier compounds after they have been oxidized in a nitro reduction reaction. The assumptions cannot be made a priori that reduction in the aqueous phase is negligible as Weber and Wolfe assume in order to simplify their model.

Recommendations

Several process level information gaps have been identified which will impede serious numerical modeling of abiotic reaction processes. The following items are presented for consideration in future experimental efforts.

Identify the reaction mechanisms responsible for abiotic reduction.
The most glaring gap in our understanding of XAC abiotic processes is the uncertainty concerning the reaction mechanisms, particularly with respect to the reducing agent and the nature of insoluble products.

Experiments with multicomponent wastewaters and inappropriately characterized soils yield results that are at best difficult to interpret. All soils are by definition poorly characterized for the purpose at hand since the key
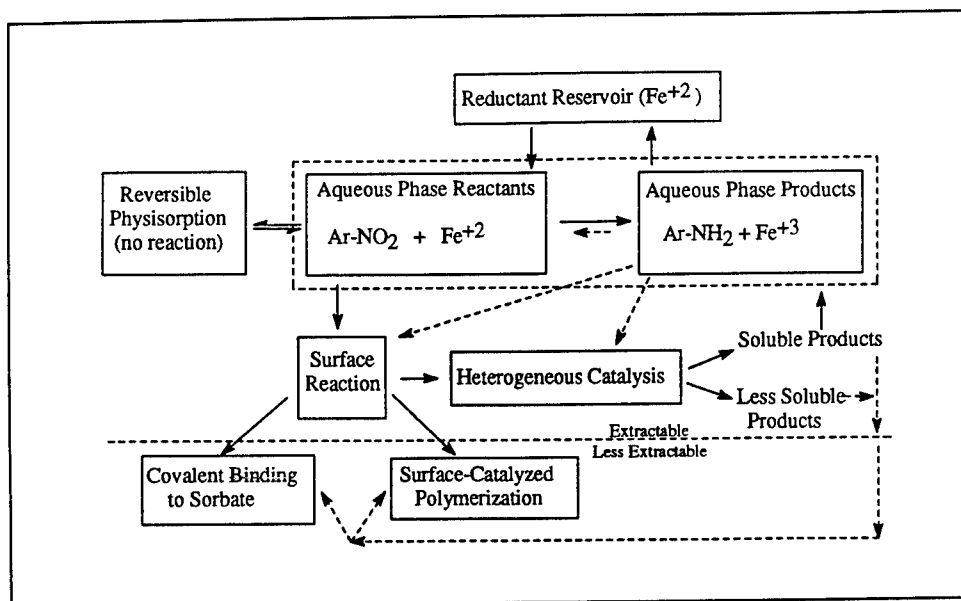
Figure 8.2. Proposed flow diagram for an abiotic reaction pathway (the Fe^{+2}/Fe^{+3} system shown is a surrogate for any electon donor system, e.g., iron porphyrins, hydroquinones)

reactants have not been identified in any system. Such experiments provide an indication as to how natural systems behave but yield little in terms of elucidating the process or controls on those reactions. The reaction mechanism will be difficult to establish without a systematic determination of the source of the mass balance "losses" that have been observed in column experiments (Pennington and Patrick 1990, Ainsworth et al. 1993).

Most researchers investigating abiotic reduction reactions have adopted the approach of examining simple mixtures in simple systems, e.g., one nitroaromatic, one electron carrier or binding substrate, all in a well characterized system. Possible reaction mechanisms are identified. Gradually the complexity of the system can approach that of the environment. Reaction mechanisms so identified provide no assurance that the mechanism will be significant in natural systems, but do lead to a more complete understanding of XAC behavior.

Evaluate homologous surrogate compounds. An alternative approach would be to characterize soil constituents as precisely as technically feasible, then conduct batch and/or column experiments with "model sorbents" which act a surrogates for various soil constituents or functional groups. For example, to assess the impact of iron oxyhydroxides, a synthetic porous medium can be constructed with either oxide coatings on spherical glass or silicon beads, or crushed, crystalline hematite or other common iron oxide mineral. Then, if reactions proceed in the presence of oxides coatings but not on pure quartz (or other mineral) surfaces, an iron-associated reaction mechanism is further implicated. If iron is being oxidized in a nitro-to-amino reduction reaction, one potential electron source will have been identified.

Use of multiple XACs in homologous series provides another avenue to resolve the influence of various substituent functional groups on fate and transport behavior. The "typical" XAC suite of interest includes some subset of TNT, DNTs (4-A-2,6-DNT, 2-A-4,6-DNT), 2,4-DA-6-NT, RDX, and HMX. If, for example, a given column breakthrough experiment also includes benzene, aniline, toluene, and/or toluidine, trends in behavior can be established. The solute suite should also include a conservative tracer as a reference solute; it is dangerous to assume RDX to be conservative for all soils.

Identify irreversibly bound surface complexes. The identity of the surface complexes or reaction products is a fundamental requirement for useful numerical simulation of the reactions. Surface reactions are difficult to substantiate by direct analysis due to the problems in resolving the new compound or complex from an often already complex, heterogeneous, organic macromolecule. Perhaps the structure or changes in structure at the reaction surface may be elucidated by applying nuclear magnetic resonance (NMR) spectroscopy (e.g., Weber, McGinley, and Katz 1992) or another powerful surface spectroscopy technique (e.g., scanning tunnel spectroscopy of sorbate on a crystalline surface). Direct identification of surface reaction mechanisms would be invaluable in deciphering the apparently irreversible sorption of XACs. Binding to humics is particularly difficult to identify by spectroscopic techniques due to the complex, heterogeneous nature of soil organics.

One alternative is the selective blocking of subsets of sites by chemical pretreatment. Parris (1980), for example, used sodium borohydrite to reduce aldehyde and ketone functional groups to alcohols. This approach will at best suggest a reaction mechanism, since it is still difficult to verify the selectivity and completeness of the blocking treatment. Another approach is to use simpler "model" compounds with homogeneous functional group, e.g., 3,4-dimethoxybenzaldehyde and 1,4-benzoquinone as surrogates for, respectively, the aldehyde and quinone functional groups of humates (Parris 1980).

Conduct studies under controlled or monitored environmental conditions. Temperature, pH, and Eh should be monitored (at least) and controlled if noninterfering buffer systems can be identified. The need to characterize more carefully the redox condition of the system (Scott and Morgan 1990) is becoming increasingly evident. An appropriate measure of the soil redox capacity as well as intensity is required.

Mathematical and numerical modeling needs

Abiotic reactions appear to be very important in XAC fate and transport in the subsurface. Predictive modeling will require identification of the reactants and products, estimates of the reaction kinetics, and environmental controls on the kinetics. There is much to do.

The specific kinds of abiotic reactions discussed above will require new code development. A multicomponent, multiprocess, hydrogeochemical model will be required to begin to describe mathematically these complex systems in order to evaluate our understanding of the key processes. Existing groundwater contaminant transport models typically describe solute "disappearance" with a first-order decay reaction, which may be adequate for simple applications, but these models are nearly useless for research application.

9 Conclusions and Recommendations

9.1 Summary and Conclusions

The ultimate goal of this and affiliated efforts is to develop accurate process descriptors for modeling the subsurface transport of explosives and explosives associated compounds (XACs). Toward this end, the goals for this report were as follows:

    a. Review conceptual and mathematical models for processes that affect the subsurface transport of XACs.

    b. Identify gaps in our understanding of these transport processes as they affect our ability to model transport and remediation.

    c. Identify key parameters and measurements required to distinguish appropriate models.

    d. Identify essential components necessary for modeling explosives transport and remediation.

    e. Recommend experimental procedures to rectify the information gaps.

The first task was to identify the subsurface processes that are known or believed to affect XACs. The scarcity of information sufficiently detailed to elucidate specific processes forced an expansion of the inquiry to include compounds of similar structure.

The processes affecting XACs reviewed include advective transport in saturated and unsaturated media, hydrodynamic dispersion, molecular diffusion, solids dissolution, equilibrium and nonequilibrium sorption, volatilization, biotransformation, abiotic reduction, abiotic binding, aqueous speciation, hydrolysis, and photolysis. The significance of each of these processes for explosives fate and transport is examined. Process descriptors are presented for most of these. Attention is focused on porous media. Parameters needed

for process descriptors and numerical models are not available for many XACs; therefore, methods to estimate these parameters have been reviewed.

Advection, dispersion, diffusion, sorption, abiotic reactions, and biotransformation are the most significant processes affecting the subsurface transport of explosives. Numerical models for explosives transport must solve descriptor equations for this minimal set of processes. Each of these is discussed briefly below, prior to identifying specific priority areas for process formulation research.

Advection-dispersion. The Darcy equation flow should be adequate for most porous media conditions likely to be encountered. The advection-dispersion transport equation is also very well established and will serve as a basis for the multiple processes affecting explosives. Multiple descriptors should be included in any model simulating unsaturated flow, including the relatively simple Richard's equation, as well as models based on the van Genuchten and/or Brooks-Corey constitutive relations (see Chapter 3).

Dissolution. A first-order dissolution kinetic descriptor or perhaps equilibrium partitioning should be adequate for preliminary efforts to model the dissolution of pure explosives. Dissolution of solid mixtures of contrasting solubility may require a more complicated descriptor, perhaps a form of a dual-region model to capture the potential diffusion-limiting effects (see Chapter 4).

Sorption. There is a multitude of sorption descriptors from which to choose. For simple sorption, a Freundlich model has general applicability. The sorption of weakly binding explosives, such as RDX and HMX, may be modeled adequately with a simple linear sorption isotherm or with a multi-component empirical model (e.g., Ainsworth et al. 1993). However, amino-bearing XACs are highly susceptible to "irreversible sorption" including covalent binding to soil components, further reduction, and polymerization to form less soluble products. In these situations, sorption models must be coupled to other process descriptors, such as for abiotic reduction. Physical nonequilibrium sorption descriptors (also affecting dispersion) should be investigated for potential application to XAC transport. The impact of cosolvents or surfactants on XAC sorption behavior is not well known (see Chapter 5).

Volatilization. Sublimation is not likely to be a very important pathway for solid explosives in the environment. Volatilization of aqueous solutes is marginally significant only for some of the lower molecular weight XACs such as nitrobenzene (see Chapter 6).

Biotransformation. Biotransformation is an important process in soils and aquifers. In situ biodegradation predominantly involves the reduction of nitro groups to amino groups in the requisite presence of a primary substrate. Evidence of natural consortia utilizing explosives as a primary carbon or energy source is lacking, though it has been reported for cultured microorganisms, in some cases derived from explosives-contaminated soils. Therefore,

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XAC bioremediation models should simulate the transport and utilization of one or more primary substrates, two or more electron acceptors (perhaps, oxygen, nitrate, and Fe[III]), one or more explosive or parent XAC transformed by cometabolism, and two or more of the reduced XAC products. Bioremediation modeling may also require additional transport equations for other additives such as surfactants, macronutrients, or additional electron acceptors. Resolution of microbially mediated reductions from abiotic reduction processes is a high priority research area, though it may not be feasible in complex natural media (see Chapter 7).

Photolysis and hydrolysis. These processes can generally be neglected in subsurface transport modeling. Photolysis is important only to account for transformation products that may subsequently leak into the subsurface (see Chapter 8).

Abiotic reduction reactions. The potential for abiotic reduction of nitroaromatic compounds in aqueous solution and at solid surfaces is established (see Chapter 8). Possible reductants and reaction mechanisms have been identified. However, the abiotic reduction of explosives in soils remains enigmatic. Experimental evidence suggests that the reduction mechanism for TNT can be very fast or negligible. Field evidence shows cases of both extensive transport and high attenuation of TNT. In light of such uncertainty, numerical modeling must adopt multiple working hypotheses, beginning with simple first-order kinetic transformation with uncertain stoichiometry. Once key soil reductants are identified and the nature of the reaction mechanism elucidated, serious modeling of abiotic reduction can begin. Resolution from microbially mediated reduction reactions will be problematic.

Binding to soil components. As with abiotic reduction, the details of covalent binding or polymerization reactions remain uncertain (see Chapter 8). Again, numerous soil components, primarily certain functional groups in soil organics, have been proposed as binding sites. There are no published data unequivocally identifying particular soil components as binding sites for explosives or any nitro- or amino-aromatics.

9.2 Research Priorities

Many gaps exist in our understanding of subsurface processes in general, particularly as relates to the effect of heterogeneities on contaminant transport and remediation processes. The subsurface behavior of explosives is less well understood than many other more common contaminants, partly because these are military unique compounds, but primarily because they are subject to multiple and complex processes that are exceedingly difficult to resolve. The following major thrust areas are proposed for future research. These have been discussed in more detail elsewhere in the text.

Identify abiotic reaction mechanisms and rates

By far, the most glaring shortcoming in our understanding of XAC-attenuating processes is the role of abiotic reactions: reduction reactions, polymerization, and covalent binding to soil compounds. Abiotic reactions appear to be very important, but the reactant soil components are only suspected based on inference from statistical correlation between soil parameters and net behavior and from limited experimental data on simple systems. Predictive modeling of these key processes would be poor at present. Fundamental research is required to identify potential reductants and binding moieties in soils. Continued research with simple systems should proceed along with efforts to evaluate multiple processes. Once mechanisms are understood, attention can shift to details of the reaction stoichiometry, kinetics, and the influence of environmental conditions.

Investigate microbial transformation and growth kinetics

Explosives and XACs are biodegradable, and the basic reaction pathways have been identified, at least for major explosives. Identifying bacteria or consortia capable of nitro elimination reactions and subsequent mineralization should clearly be a high priority. Environmental controls on the multiple intermediate reactions are poorly known. Effective remediation design and numerical simulation require knowledge of the rate-limiting processes under various remediation strategies and environmental conditions. Establishing microbial preferences (biodegradability) for multiple XACs by either experiment or estimation with empirical quantitative structure-property relationships (QSARs) would also be very useful in predicting XAC transport. Stimulating desirable in situ bioreactions by introducing additives (e.g., substrates, electron acceptors, nutrients, surfactants) also requires a level of understanding not yet realized.

Evaluate the influences of media heterogeneities on transport and remediation processes

Physical, chemical, and microbial heterogeneities exist at multiple scales within soils and aquifers. Processes investigated at the bench scale are generally conducted with the assumption that results will be applicable in the field. Unless proper account is taken of the potential influence of heterogeneities (i.e., scaling), this assumption may not be valid. The impacts of field-scale, hydrogeologic heterogeneities, and how best to incorporate them in numerical models are arguably the most important unresolved issues regarding advective transport. Appropriate scaling techniques for the processes affecting explosives are not available.

Experiments are required at the bench scale (homogeneous, aggregate or undisturbed, heterogeneous core), meso-scale (e.g., an engineered heterogeneous artificial aquifer or field soil block), and field scale (soils,

aquifers) to provide information on which processes are important at various scales.

Thoroughly characterize media and solutes

In light of the considerable uncertainty regarding the specifics of abiotic processes affecting explosives, all experiments evaluating the fate of XACs in natural soils should include a thorough analysis of the soil components. The thorough analyses suggested here are well beyond the normal characterization of soils with respect to, for example, total organic carbon, extractable iron, clay content, though these should be measured as well. The organic carbon fraction should be analyzed as quantitatively as feasible for its constituent functional groups that may act as reductants or covalent binding sites. Clay mineralogy may be more important in XAC transport than a clay size particle analysis. Extractable iron determinations do not reveal the mineralogy (or chemistry) of the soil iron, which may be relevant. Other metals may be important as well. Experiments should also monitor all potentially important environmental variables, such as pH, Eh, major cation concentrations, temperature, flow rate (if appropriate), as well as all XAC components introduced or produced.

Numerical model development

No commercially available code currently available can simulate all the processes known or strongly suspected of controlling XAC transport. There may be a few research codes that can model parts of the problem. Any number of numerical codes can make XACs "disappear" to fit limited observations without consideration of underlying mechanism.

The greatest challenge in process description and numerical modeling will be in merging of the individual process models into a single model that addresses issues of multiple, coupled, reaction mechanisms—abiotic and microbial reduction, sorption, etc. Only then can the processes and parameters identified under well-controlled laboratory conditions hope to be applied successfully in the field. Numerical modeling is undoubtedly the most effective way to integrate such a complex suite of processes.

Secondary research priorities

Develop parameter estimation methods for explosives. Where possible, all descriptor parameters should be determined based on experimental data. However, it is anticipated that not all required parameters, particularly thermodynamic parameters such as infinite dilution activity coefficients, are available for all explosives contaminants. Data as fundamental as aqueous solubility may not be readily available (or reliable) for some of the many alteration compounds. Even where experimental data are available,

independent means for parameter corroboration is always desirable. New explosives will be developed (e.g., Borman 1994) for which environmental parameters may not be available or may be prohibitively expensive to determine. Yet if transport modeling of these solutes is deemed necessary, model parameters must be estimated. Numerous nonexperimental techniques exist or are developing for environmental parameter estimation, such as the following:

a. Quantitative Structure—Activity (QSAR) and Structure-Property (QSPR) Relations for (1) simple correlations such as solubility-$K_{o/w}$ or others, some of which are presented in this report; and (2) biodegradability, biouptake, and toxicity.

b. Group-contribution models (e.g., UNIFAC/UNIQUAC, NRTL, ASOG) with which to estimate activity coefficients, partition coefficients, etc., from molecular structure.

c. Molecular interaction simulation models; ab initio studies.

These approaches have produced useful results with other classes of contaminants and should be explored for application to explosives.

Investigate cosolvency effects. Cosolvency or enhanced solubilization effects for explosives transport are largely unknown beyond the possible use of surfactants to enhance bioavailability. These effects should be assessed not only as to how natural dissolved organic solutes may affect explosives transport, but also as to the feasibility of utilizing enhanced solubilization as a remediation technique for in situ or ex situ soil washing.

Set up an on-line database for process parameter information. There is a wealth of information dispersed in technical documents prepared by or for WES, CRREL, BRDL, and AEC (THAMA) regarding environmental aspects of explosives. This information would be of much greater utility to DOD personnel if it were organized into a single database. The database could include the best available information regarding (a) basic chemical and physical properties, (b) measured and estimated parameters needed for numerical simulation, (c) identification of field parameters that require monitoring to support various levels of process description, and (d) remediation technologies applicable for explosives. The data must be readily retrievable, perhaps from an electronic bulletin board accessed via the Internet. The database could eventually include similar information for other contaminants of concern to the DOD. Alternatively, the XACs database could be appended to existing bulletin board databases, such as the Navy Environmental Bulletin Board System (NEBBS) or one of EPA's bulletin boards.

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Appendix A
Physical, Chemical, and Environmental Data

Physical, chemical, and environmental data for representative explosives and XAC's are presented in a series of tables as follows:

Table A1: RDX
Table A2: HMX
Table A3: 2,4,6-TNT
Table A4: 2,4-DNT and 2,6-DNT
Table A5: 1,3,5-TNB
Table A6: 1,3-DNB
Table A7: Tetryl

These tables are perceived by the author to be living documents, subject to change and evolution as more becomes known about processes affecting the subsurface transport of XAC's. Tables are not presented for certain XAC's for which there are simply too few data available, such as the amino-nitroaromatic alteration products of TNT. The author will continue to maintain a database of measured or estimated parameters deemed useful for numerical modeling of XAC transport in groundwater. Interested readers are invited to contact the author to submit new information or to obtain an updated version of the tables (internet = cjm@hvorslev.wes.army.mil; WPOffice = mcgratc@elmd.wes.army.mil; phone = 601-634-3798; FAX = 601-634-3129).

Table A1
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) Physical, Chemical, and Environmental Properties

CAS No.: 121-82-4

Other names: hexogen; cyclotrimethylenetrinitramine; cyclonite; RDX ≡ Royal Demolition eXplosives (or Research & Development eXplosives)

Formula (semistructural and empirical): $(NO_2)_3N_3C_3H_6$ or $C_3H_6N_6O_6$

Molecular Mass: 222.26 $g \cdot mol^{-1}$
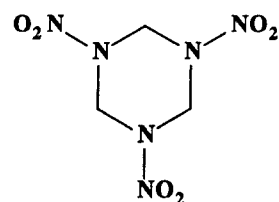
Parameter	Value / Comments	Reference
Density	1.82 $g \cdot cm^{-3}$	Kaye (1980)
Melting Point	204-206 °C	Meyer (1977); Banerjee, Yalkowsky, and Valvani (1980); Merck (1983)
Crystallography	Orthorhombic crystals (from acetone); colorless	Verschueren (1983), Meyer (1977)
Dipole Moment	Low (≈ 0); molecule is nearly symmetrical (out of plane configurations have non-zero dipole moment)	
Vapor Properties (RDX)		
Henry's Law Constant, K_H	1.96 E-11 $atm \cdot m^3 \cdot mol^{-1}$ (25 °C; est.) 2 E-05 $torr \cdot L \cdot mol^{-1}$ (°C; est.)	Rosenblatt et al. (1989) Spanggord et al. (1980a,b)
Vapor Pressure	4.03 E-09 torr (25 °C; est.)	Rosenblatt et al. (1989)
Aqueous Solubility (RDX)		
10 °C	28.9 ± 1.0 $mg \cdot L^{-1}$	Sikka et al. (1980)
20 °C 25 °C (?) 25 ± 0.2 °C	42.3 ± 0.6 $mg \cdot L^{-1}$ 45 $mg \cdot L^{-1}$ 59.9 ± 1.2 $mg \cdot L^{-1}$; 269 μM	Sikka et al. (1980) Spalding and Fulton (1988) Banerjee, Yalkowsky, and Valvani (1980)
26.5 °C	59.9 ± 1.4 $mg \cdot L^{-1}$	Sikka et al. (1980)
30 °C	75.7 ± 1.1 $mg \cdot L^{-1}$	Sikka et al. (1980)
EPA Drinking Water Std. (DWEL)	0.10 $mg \cdot L^{-1}$	(from Rosenblatt et al., 1989)
RMCL Recc.Max.Contam.Lev.	35 $\mu g \cdot L^{-1}$	DOA (1980; from Spalding and Fulton 1988)
Solubility in Organic Solvents (RDX)		
Acetone	1 g / 25 mL (40 000 $mg \cdot L^{-1}$) 4.18 g / 100 g @ 0 °C 8.38 g / 100 g @ 30 °C	Merck (1983) Etnier (1986)
Benzene	0.055 g / 100 g @ 25 °C 0.085 g / 100 g @ 30 °C	Etnier (1986)
Toluene	0.016 g / 100 g @ 0 °C 0.025 g / 100 g @ 25 °C 0.050 g / 100 g @ 30 °C	Etnier (1986)

(Continued)

Table A1 (Concluded)

Parameter	Value / Comments	Reference
Solubility in Organic Solvents (RDX) (Continued)		
Methanol	0.140 g / 100 g @ 0 °C 0.325 g / 100 g @ 30 °C	Etnier (1986)
Ethanol	0.040 g / 100 g @ 0 °C 0.155 g / 100 g @ 30 °C	Etnier (1986)
Acetic Acid (glacial)	slight	Merck (1983)
Environmental Fate & Transport (RDX)		
Partitioning Coefficients	$\log k_{ow}$: 0.87 ± 0.028 0.81 0.86 1.1	Banerjee, Yalkowsky, and Valvani (1985) Major (1989) Jenkins (1989) Leo, Hansch, Elkins (1971)
	$\log k_{oc}$: 2.00 2.13 0.89, 1.87, and 2.43 1.62 and 2.10	Rosenblatt (1986; CAAP) Tucker et al. (1985) Sikka et al. (1980) Spanggord et al. (1980b)
	k_d: 0.2, 1.8, 6.4, and 7.8 0.8, 3.06, and 4.15 1.4 and 4.2 1.6 (nondimensional; kg-water / kg-soil); CAAP aquifer material with very low f_{oc}	Hale, Stanford, and Taft (1979) Sikka et al. (1980) Spanggord et al. (1980b) Tsai, Davis, and Benioff (1985)
Diffusion	Water: 7.15 E-06 cm² · s⁻¹ Air: 0.074 cm² · s⁻¹	Rosenblatt et al. (1989)
Biodegradability	Aerobic: negligible	McCormick, Cornell, and Kaplan (1981)
	Anaerobic: significant cometabolism Transformation products: methanol, hydrazine, formaldehyde, dimethylhydrazine (1,1-, 1,2-) which are mutagens	McCormick, Cornell, and Kaplan (1981)
Toxicity	Possible carcinogen (USEPA); not mutagen; transformation products may be toxic	McCormick, Cornell, and Kaplan (1981)
Photosensitivity	Rapid; not enhanced by humics substrate (sensitizer) Transformation products: nitrite, nitrate, formaldehyde, N_2, triazine (?)	Sikka et al. (1980) McCormick, Cornell, and Kaplan (1981)
Hydrolysis	Insignificant	Rosenblatt et al. (1989)
Other Abiotic Reactions		
Aqueous Speciation	Not likely.	—
Aqueous Complexation	No reports; probable, but weak.	—
Abiotic Reduction	No reports; perhaps under anaerobic systems; probably not under aerobic conditions.	—
Polymerization	No reports; perhaps in reduced (amino compounds) transformation products.	—
Binding to Soil Solids	No reports; perhaps amino compounds.	—

Appendix A   Physical, Chemical, and Environmental Data

Table A2
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) Physical, Chemical, and Environmental Properties

CAS No.: 2691-41-0
Other names: Octagon; cyclo.tetramethylene.tetranitramine
Formula (semistructural and empirical): $C_4H_8N_4(NO_2)_4$ or $C_4H_8N_8O_8$
Molecular Mass: 296.2 g mol^{-1}
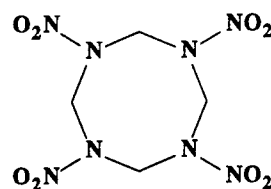
Parameter	Value / Comment	Reference
Density	1.90 g cm^{-3} (β form)	Rosenblatt et al. (1989)
Melting Point	286 °C	Rosenblatt et al. (1989)
Crystallography	Colorless crystals	Meyer (1977)
Dipole Moment	Low ($\approx$ 0); molecule is nearly symmetrical; non-zero DM may arise from out of plane configurations	—
Vapor Properties (HMX)		
Henry's Law Constant, K_H	2.60 E-15 atm m^{-3} mol^{-1} (25 °C; est.)	Rosenblatt et al. (1989)
Vapor Pressure	25 °C 3.33 E-14 torr 100 °C 3 E-09 torr	Rosenblatt et al. (1989) Tucker et al. (1985)
Aqueous Solubility (HMX)		
10 °C	1.21 ± 0.04 mg·L^{-1}, 4.09 μM	Spanggord et al. (1982b)
20 °C	2.6 ± 0.01 mg·L^{-1} , 8.78 μM	Spanggord et al. (1982b)
22-25 °C	5 mg·L^{-1} 16.8 μM	Glover & Hoffsommer (1973)
30 °C	5.7 ± 0.1 mg·L^{-1} , 19.2 μM	Spanggord et al. (1982b)
Solubility in Organic Solvents (HMX)		
Acetone	n.d.	—
Benzene	n.d.	—
Ethanol	n.d.	—
Acetic Acid (glacial)	n.d.	—
Environmental Fate & Transport (HMX)		
Partition Coefficients	log K_{ow}: 0.26 0.06	Major (1989) Jenkins (1989)
	log K_{oc}: 0.54 (est.) log K_{oc}: 2.83; for Holston River sediment (f_{oc}=0.013) based on measured k_p = 8.7	Rosenblatt et al. (1989); Spanggord et al. (1982b)
	K_d: n.d.	—
	K_B: 63 (measured biosorption partitioning)	Spanggord et al. (1982b)

(Continued)

Table A2 (Concluded)

Parameter	Value / Comment	Reference
Environmental Fate & Transport (HMX) — Continued		
Volatilization	Minor; k_v = 2.4 E-04 to 7.2 E-04 day^{-1} (1st-order rate constant); $t_{1/2}$ = 3000 to 1000 days (est. from experiments)	Spanggord et al. (1982b)
Diffusion	Water: 6.02 E-06 cm$^2 \cdot$s^{-1} (est.) Air: 0.063 cm$^2 \cdot$s^{-1} (est.)	Rosenblatt et al. (1989)
Biodegradation	Aerobic: negligible	Spanggord et al. (1982b)
	Anaerobic: slow; accelerated, 1° kinetics in the presence of primary substrate (cometabolism)	Spanggord et al. (1982b)
Toxicity	Not carcinogenic	(in Rosenblatt et al., 1989)
Photolysis	Significant; 1st-order k = 0.15 d^{-1} ($t_{1/2}$ = 5 d); for Hoston River water	Spanggord et al. (1982b)
Hydrolysis	Not significant	Spanggord et al. (1982b)
Other Abiotic Reactions		
Aqueous Speciation	Not likely.	—
Aqueous Complexation	No reports; probable, but weak.	—
Abiotic Reduction	Not under aerobic conditions; perhaps in anaerobic systems.	Spanggord et al. (1982b)
Polymerization	No reports; perhaps in reduced transformation products (amino compounds).	—
Binding to Soil Solids	No reports; perhaps in amino reduced compounds.	—

Appendix A   Physical, Chemical, and Environmental Data

Table A3
2,4,6-trinitrotoluene (TNT) Physical, Chemical, and Environmental Properties

CAS Reg. No.: 118-96-7
Other names: α-trinitrotoluene, sym-trinitrotoluene,
    1-methyl-2,4,6-trinitrobenzene
Formula (semistructural, empirical): $C_6H_2CH_3(NO_2)_3$ or $C_7H_5N_3O_6$
Molecular Mass: 227.13 g·mol^{-1}
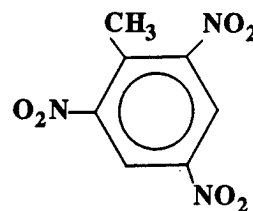
Parameter	Value / Comment	Reference
Density	1.654 g·cm^{-3} 1.654 - 1.663 g·cm^{-3}	Dean (1985) Urbanski (1964)
Melting Point	80.1 °C 80.65 °C	Dean (1985) Urbanski (1964)
Crystallography	Monoclinic rhombohedra from ethanol: colorless Commercial form: yellow needles or columns	Verschueren (1983) Merck (1983)
Dipole Moment	1.37 D	Merck (1983)
Vapor Properties (TNT)		
Henry's Law Constant, K_H	0.18 torr L mol^{-1} < 0.02 torr L mol^{-1} 1.1 E-08 atm·m^3·mol^{-1} [25 °C]	Spanggord et al. (1980a) Haynes and Smith (1981) Rosenblatt et al. (1989)
Vapor Pressure (solid)	20.0 °C 1.28 E-06 torr 25 °C 5.51 E-06 torr (est.)	Leggett, Jenkins, and Murrmann (1977) Rosenblatt et al. (1989)
Aqueous Solubility (TNT)		
0 °C	100 mg·L^{-1}	Urbanski (1964)
10 °C	110 mg·L^{-1}	Urbanski (1964)
15 °C	200 mg·L^{-1} 120 mg·L^{-1}	Verschueren (1983) Urbanski (1964)
20 °C	130 mg·L^{-1}	Urbanski (1964)
25 °C	~100 mg·L^{-1} (~0.01%) 150 mg·L^{-1}	Merck (1983) Urbanski (1964)
Hygroscopy	Non-hygroscopic; 0.05% water	Urbanski (1964)
EPA Drinking Water Std. (DWEL)	0.020 mg·L^{-1}	(in Rosenblatt et al. 1989)
RMCL (Recc. Max. Contam. Lev.)	44 μg·L^{-1}	DOA (1980; Spalding and Fulton, 1988)

TNT Solubility in Organics Solvents [g L^{-1}]

	10 °C	15 °C	20 °C	25 °C	
Acetone	780	920	1090	1320	Urbanski (1964)
Benzene	360	500	670	880	"
Toluene	380	450	550	670	"
Ethanol (95%)	8.5	10.7	12.3	14.8	"

(Continued)

Table A3 (Concluded)

Parameter	Value / Comment	Reference
	Environmental Processes (TNT)	
Partitioning Coefficients	$\log K_{ow}$ = 2.06 ; 1.86	Rosenblatt et al. (1989), Jenkins (1989)
	$\log K_{oc}$ = 2.72	Rosenblatt (1986)
	K_d = 53 ± 20 mL·g^{-1} 2 - 56 mL·g^{-1}	Spanggord et al. (1980a)
Diffusion	Water: 6.71 E-06 cm^2·s^{-1} (25 °C; est.) Air: 0.064 cm^2·s^{-1} (25 °C; est.)	Rosenblatt et al. (1989)
Biotransformation	Major process in surface and ground waters. Successive reduction of nitro (R-N[+V]O$_2$) to amine (R-N[-I]H$_2$) groups is most common.	Rosenblatt et al. (1989)
	A few reports of microbial growth on and mineralization of TNT *via* elimination reactions; these microorganisms use TNT as the sole nitrogen, and carbon source.	Boopathy and Kulpa (1992), Duque et al. (1993), Unkefer et al. (1990)
	Half-life in groundwater (est.): 8640 hr (12 mo.) to 672 hr (4 weeks).	Howard et al. (1991)
	Aerobic: Major transformation process in surface water; significant in soils as well; slow rates Products: hydroxamino and azoxytoluene compounds	Kaplan and Kaplan (1982) Spanggord et al. (1980a)
	Anaerobic: Primarily nitro-to-amino reduction; moderate rates	
Toxicity	EPA possible human carcinogen; May absorb through skin; can cause headache, weakness, anemia, liver injury; Vapors are toxic.	(in Rosenblatt et al., 1989); Merck (1983)
Photosensitivity	Significant. To: 2,4,6-trinitrobenzaldehyde, 1,3,5-trinitrobenzene, 3,5-dinitroaniline, 2-amino-4,6-dinitrobenzoic acid, azoxydicarboxylic acid	Kaye (1980), Burlinson (1980)
Hydrolysis	Alkaline sensitive	
Other Abiotic Reactions		
Aqueous Speciation	Not likely.	—
Aqueous Complexation	Forms complexes with surfactants.	Kaplan and Kaplan (1982)
Abiotic Reduction	Apparent major reaction pathway; anaerobic or aerobic conditions.	—
Polymerization	No reports. Reduction products may form azo or azoxy compounds *via* amino intermediates.	—
Binding to Soil Solids	No reports for XACs. Some data for similar compounds. Reduction products appear to bind with carboxyl and/or other functional groups in soil organics (by analogy to aniline).	Weber et al. 1992; Wolfe and Macalady 1992; Bollag, Minard, and Liu et al. 1983; Parris 1980; Hsu and Bartha 1974.

Table A4
2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT) Physical, Chemical, and Environmental Properties
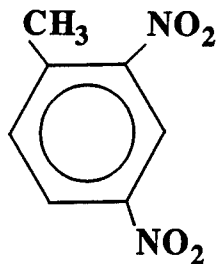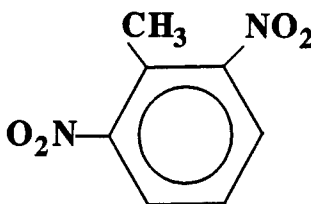
	2,4-DNT CAS: 121-14-2	2,6-DNT CAS: 606-20-2	
Structure			Other Names: 1-methyl-2,4- (or 2,6-) dinitrobenzene

Formula (semistructural, empirical): $C_6H_3CH_3(NO_2)_2$ or $C_7H_6N_2O_4$
Formula Weight: 182.14 $g \cdot mol^{-1}$

Parameter	Value / Comment		Reference
Density	1.521 $g \cdot cm^{-3}$ [4 °C] 1.379 $g \cdot cm^{-3}$ [20 °C]	1.538 $g \cdot cm^{-3}$ [°C]	Montgomery and Welkom (1990); Verschueren (1983)
Melting Point	70 °C 70.5 °C 71 °C 64-65 °C	64-66 °C — 65.5 °C 64-65 °C	Verschueren (1983) Meyer (1977) Urbanski (1964) Dean (1985)
Crystallography	Pale yellow to red needles		Meyer (1977)
Dipole Moment	n.d.	n.d.	
Vapor Properties (DNT's)			
Henry's Law Constant K_H	3.4. $torr \cdot L \cdot mol^{-1}$ 0.45 ±0.04 $torr \cdot L \cdot mol^{-1}$ 0.34 ±0.05 $torr \cdot L \cdot mol^{-1}$ 1.86 E-07 $atm \cdot m^3 \cdot mol^{-1}$ (25 °C) 8.67 E-07 $atm \cdot m^3 \cdot mol^{-1}$	— — — 4.86 E-07 $atm \cdot m^3 mol^{-1}$ (25 °C) 2.17 E-07 $atm \cdot m^3 mol^{-1}$ (°C)	Spanggord et al. (1980a) Haynes and Smith (1981) Haynes and Smith (1981) Rosenblatt et al. (1989) Montgomery and Welkom (1989)
Vapor Pressure	20 °C 1.3 E-04 torr (meas.) 25 °C 2.17 E-04 torr (est.) 35 °C 0.014 mbar 8.67 E-07 atm	20 °C 1.35 E-04 torr (meas.) 25 °C 5.67 E-04 torr (est.) —	Pella (1977) Rosenblatt et al. (1989) Meyer (1977)
Aqueous Solubility (DNT's)			
15 °C	n.d.	n.d.	--
22 °C	270 mg L^{-1}	---	Montgomery and Welkom (1989)

(Continued)

Table A4 (Concluded)

Parameter	Value / Comment		Reference
Aqueous Solubility (DNT's) (Continued)			
25 °C	280 mg L^{-1} (est. by interp.) ---	--- 208 mg/L	Kaye (1980) Rosenblatt et al. (1989)
Solubility in Organic Solvents (DNT's)			
Acetone	—	—	—
Benzene	—	—	—
Toluene	—	—	—
Ethanol (95%)	—	—	—
Environmental Parameters (DNT's)			
Partitioning Coefficient	log K_{ow} = 1.98	log K_{ow} = 1.89 = 2.02	Hansch and Leo (1979) Jenkins (1989)
	log K_{oc} = 1.79 (est.) 2.40	log K_{oc} = 1.79 (est.) 1.89 (est.)	Montgomery and Welkom (1989); Rosenblatt et al. (1989)
	log K_d = n.d.	log K_d = n.d.	
Diffusion Coefficients	Water: 7.31 E-06 cm^2·s^{-1} [est.] Air: 0.067 cm^2·s^{-1} [est.]		Rosenblatt et al. (1989)
Biotransformation	Mineralization of DNTs reported; reduction reactions		Spanggord et al. (1980a)
	Half-life (est.) in groundwater: 8640 hr (12 mo.; anaerobic) to 48 hr (2 d; aerobic) Half-life (est.) in soil: 4320 d (6 mo.) to 472 d (4 wk)		Howard et al. (1991)
Toxicity	EPA probable human carcinogen	-----	(in Rosenblatt et al., 1989)
Photosensitivity	Photolysis: aquatic half-life = 72-23 hr Photooxidation: aquatic half-life = 33-3 hr	Photolysis: --- Photooxidation: ---	Howard et al. (1991) Mill and Mabey (1985) Spanggord et al. (1980a); Simmons and Zepp (1986)
Hydrolysis	n.d.	n.d.	n.d.
Other Abio. Rxns.: Aq. Speciation Aq. Complexation Abiotic Reduction Polymerization Binding to Soil Solids	 Not likely. No data. May, like TNT, form complexes with surfactants. No data. Likely significant reaction pathway; anaerobic or aerobic conditions. No reports. Reduction products may form azo or azoxy compounds via amino intermediates as does TNT. No reports. Reduction products appear to bind with carboxyl and/or other functional groups in soil organics (by analogy to aniline).		

Appendix A   Physical, Chemical, and Environmental Data

Table A5
1,3,5-trinitrobenzene (TNB) Physical, Chemical, and Environmental Properties

CAS Reg. No.: 99-35-4
Other names: *sym*-trinitrobenzene

Formula (semistructural, empirical): $C_6H_3(NO_2)_3$ or $C_6H_3N_3O_6$
Molecular Mass: 213.11 g·mol^{-1}
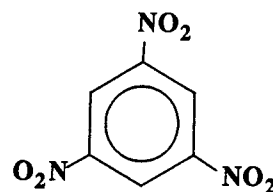
Parameter	Description	Reference
Density	1.688 (20 °C)	Dean (1985)
	1.654-1.663	Urbanski (1964)
Melting Point	122.5 °C	Dean (1985), Merck (1983)
	122 °C	Urbanski (1964)
Crystallography	Orthorhombic, bipyrimidal plates from glacial acetic acid	Merck (1983)
Dipole Moment	~0 (symmetry)	---
Vapor Properties (TNB)		
Henry's Law Constant, K_H	2.21 E-09 atm m^3 mol^{-1}	Rosenblatt et al. (1989)
Vapor Pressure (solid)	3.03 E-06 torr (25 °C; est.); Can sublimate with careful heating	Rosenblatt et al. (1989); Merck (1983)
Aqueous Solubility (TNB)		
15 °C	–	
20 °C	–	
~25 °C	~350 mg·L^{-1} (0.035 g / 100 g-water)	Merck (1983);
25 °C	385 mg·L^{-1}	Rosenblatt et al. (1989)
Solubility in Organics (TNB)		
Acetone	–	
Benzene	6,200 mg L^{-1}	Merck (1983)
Toluene	–	
Ethanol (95%)	1,900 mg L^{-1}	Merck (1983)
Environmental Processes (TNB)		
Partitioning Coefficients	K_d:	
	log K_{ow}: 1.18	Hansch and Leo (1979)
	log K_{oc}: 1.30 (est.)	Rosenblatt et al. (1989)
Diffusion Coefficient	Water: 7.20 E-06 cm s^{-1} Air: 0.068 cm s^{-1}	Rosenblatt et al. (1989)
Biodegradation	Probable. Similar to TNT, reduction and perhaps elimination of the nitro group.	–
Toxicity	–	–

(Continued)

Table A5 (Concluded)

Parameter	Description	Reference
Environmental Processes (TNB) (Continued)		
Photosensitivity	TNB is photostable. TNB is one phototransformation product of TNT in natural waters.	Rosenblatt et al. (1989); Burlinson (1980)
Environmental Processes (TNB)		
Hydrolysis	Reacts with alkalis readily	Urbanski (1964)
Other Abiotic Reactions		
Aqueous Speciation	Not likely.	–
Aqueous Complexation	May form complexes with surfactants (analogy to TNT).	–
Abiotic Reduction	No data. Probably a significant reaction pathway; anaerobic or aerobic conditions.	–
Polymerization	No reports. Reduction products may form azo or azoxy compounds via amino intermediates.	–
Binding to Soil Solids	No reports. Reduction products could bind with carboxyl and/or other functional groups in soil organics (by analogy to aniline).	–

Appendix A   Physical, Chemical, and Environmental Data

Table A6
1,3-dinitrobenzene (1,3-DNB) Physical, Chemical, and Environmental Properties

CAS Reg. No.: 99-65-0
Other names: meta-dinitrobenzene
Formula (semistructural, empirical): $C_6H_4(NO_2)_2$ or $C_6H_4N_2O_4$

Molecular Mass: 168.11 g mol⁻¹
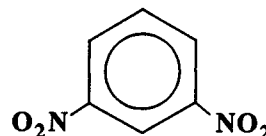
Parameter	Characteristic	Reference
Density	1.574 g cm⁻³ (18 °C)	Dean (1985)
Melting Point	89-90 °C	Dean (1985)
Crystallography	Colorless to pale yellow crystals	Verschueren (1983)
Dipole Moment	n.d.	–
Vapor Properties		
Henry's Law Constant, K_H	8.01 E-07 atm·m³·mol⁻¹ (25 °C; est.)	Rosenblatt et al. (1989)
Vapor Pressure	25 °C 1.93 E-04 torr (est.) Volatile with steam, boils at 300-303 °C	Rosenblatt et al. (1989); Merck (1983)
Aqueous Solubility (1,3-DNB)		
15 °C	469 mg·L⁻¹	Verschueren (1983)
20 °C	200 mg·L⁻¹ 180 mg·L⁻¹	Urbanski (1964) Layton et al. (1987)
25 °C	533 mg·L⁻¹	Rosenblatt et al. (1989)
Solubility in Organics (1,3-DNB)		
Acetone	– (°C)	–
Benzene	39.45 mg·L⁻¹ (18.2 °C)	Urbanski (1964)
Toluene	30.66 mg·L⁻¹ (16.5 °C)	Urbanski (1964)
Ethanol (95%)	3.5 mg·L⁻¹ (20.5 °C)	Urbanski (1964)
Environmental Parameters (1,3-DNB)		
Partition Coefficients	log K_{ow}: 1.49	Hansch and Leo (1979), Leo, Hansch, and Elkins (1971), Verschueren (1983)
	log K_{oc}: 1.56 (est.)	Rosenblatt et al. (1989)
	K_d : . –	–
Diffusion Coefficients	Water: 7.94 E-06 cm²·s⁻¹ (25 °C; est.) Air: 0.073 cm²·s⁻¹ (25 °C; est.)	Rosenblatt et al. (1989)
Biodegradation	Aerobic: mineralization observed with 13DNB as primary substrate Anaerobic:	Spanggord et al. (1980b)
	Half-life (est.) in soils: 4320 – 672 hr (6 mo. – 4 wk) Half-life (est.) in groundwater: 8640 hr (360 days)	Howard et al. (1991)
Toxicity	Mutagenic (Ames screening)	McGregor et al. (1980)

(Continued)

Table A6 (Concluded)

Parameter	Characteristic	Reference
Environmental Parameters (1,3-DNB) (Continued)		
Photosensitivity	Photolysis rate constants: 0.03 d^{-1} (distilled water), 0.029 and 0.043 d^{-1} (river water with fulvic acid)	Simmons and Zepp (1986)
Environmental Processes (1,3-DNB)		
Hydrolysis	Sensitive to alkalis	Urbanski (1964)
Other Abiotic Reactions		
Aqueous Speciation	Not likely.	–
Aqueous Complexation	No data. May form complexes with surfactants as does TNT.	–
Abiotic Reduction	No data. Probably a significant reaction pathway; anaerobic or aerobic conditions.	–
Polymerization	No reports. Reduction products may form azo or azoxy compounds via amino intermediates.	–
Binding to Soil Solids	No reports. Reduction products appear to bind with carboxyl and/or other functional groups in soil organics (by analogy to aniline).	–

Table A7
N,2,4,6-tetranitro-N-methylaniline (Tetryl) Physical, Chemical, and Environmental Properties

CAS Reg. No.: 479-45-8
Other names: nitramine, N-methyl-N,2,4,6-tetranitrobenzenamine;

Formula (semistructural, empirical):
   $(NO_2)_3C_6H_2N(CH_3)NO_2$ or $C_7H_5N_5O_8$
Molecular Mass: 287.17 g mol^{-1}
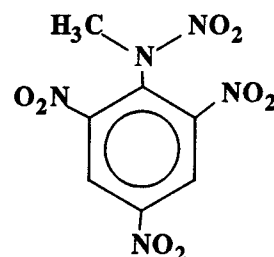
Parameter	Description	Reference
Density	1.57 (19 °C)	Verschueren (1983)
	1.73 (25 °C)	Rosenblatt et al. (1989; ref.)
Melting Point	130 °C	Verschueren (1983)
	129.5 °C	Rosenblatt et al. (1989; ref.)
Crystallography	Yellow crystals	Verschueren (1983)
Dipole Moment	---	
Vapor Properties		
Henry's Law Constant, K_H	25 °C 2.69 E-11 atm m^3 mol^{-1} (est.)	Rosenblatt et al. (1989)
Vapor Pressure	25 °C 5.69 E-09 torr (est.)	Rosenblatt et al. (1989)
Aqueous Solubility (Tetryl)		
15 °C	–	–
20 °C	–	–
25 °C	80 mg·L^{-1}	Urbanski (1964)
Solubility in Organics (Tetryl)		
Acetone	–	–
Benzene	–	
Toluene	–	
Environmental Processes (Tetryl)		
Partitioning Coefficients	log K_{ow} = 1.65	Jenkins (1989)
	log K_{oc} = 1.69 (est.)	Rosenblatt et al. (1989)
	log K_d =	–
Diffusion	Water: 5.99 cm^2 sec^{-6} (est.) Air: 0.059 cm^2 sec^{-1} (est.)	Rosenblatt et al. (1989)
Biodegradation		
Toxicity	Mutagenic (Ames screening)	McGregor et al. (1980), Whong, Speciner, and Edwards (1980)

(Continued)

Table A7 (Continued)		
Parameter	**Description**	**Reference**
Environmental Processes (Tetryl) (Continued)		
Photosensitivity	Significant; slowly in sunlight (essentially complete by 20 days)	Rosenblatt et al. (1989)
Environmental Processes (Tetryl)		
Hydrolysis	Slow; at buffered pH 9, essentially complete hydrolysis in 90 days. Products: methylnitramine, picrate ion.	Kayser, Burlinson, and Rosenblatt (1984) Rosenblatt et al. (1989)
Other Abiotic Reactions		
Aqueous Speciation	No data; not likely.	–
Aqueous Complexation	No data; may possibly form complexes with surfactants (by analogy to TNT).	–
Abiotic Reduction	No data. Probably a significant reaction pathway (anaerobic or aerobic).	–
Polymerization	No reports. Reduction products may form azo or azoxy compounds via amino intermediates.	–
Binding to Soil Solids	No reports. Reduction products appear to bind with carboxyl and/or other functional groups in soil organics (by analogy to aniline).	–

Appendix B
Solubility Correlations

    Appendix B includes two tables. Table B1 summarizes empirical correlations established between octanol/water partitioning coefficients and aqueous solubility. Table B2 relates organic carbon/water partitioning for hydrophobic organic compounds (mostly nonpolar) and aqueous solubility. These simple correlations are used to estimate for poorly characterized solutes (e.g., if only solubility data are available) environmental soil-water partitioning coefficients based on soil organic carbon (see Section 5.2).

Table B1
Summary of Empirical Expressions (Correlations) Relating Octanol-Water Partitioning Coefficient (K_{ow}) to Aqueous Solubility as Concentration (S_w, in mol·L^{-1}, Unless Otherwise Stated) or Mole Fraction (X)

Expression[1] $\log K_{ow} = \ldots$	Correlation Coefficient (r^2)	Compound Types[2]	Reference
$= 6.5 - 0.89 \log S_w - 0.015$ MP	0.96	chlorinated aromatics and aliphatics, RDX; $n = 27$	Banerjee, Yalkowsky, and Valvani (1980)
$= 5.00 - 0.670 \log S_w$ (S in μM·L^{-1})	0.985	Cl and PO_4 pesticides, PCBs; $n = 34$	Chiou et al. (1977), Chiou (1981)
$= 0.710 + 0.862 \log S_w$ (S in μM·L^{-1})	0.984	aromatic liquids and solids (as supercooled liquids); $n = 36$	Chiou (1981)
$= 0.730 - 0.747 \log S_w$	0.935 (sd=0.472)	various, low M.W. liquid organics; $n = 156$	Hansch, Quinland, and Lawrence (1968)[3], Chiou (1981)
$= 0.700 - 0.824 \log S_w$	0.955 (sd=0.344)	various, low M.W. liquid organics; $n = 111$	Yalkowski and Banerjee (1992); corrected data of Hansch et al. (1968)[3]
$K_{ow}{}^S = K_{ow}{}^O$ EXP[3.8E-2 $K_s S_w$] (K_s = salinity factor)	—	aromatic hydrocarbons in Tamar Estuary (England) sediments; $n = 9$	Harris, Balc, and Byrne (1984); salinity effects on K_{ow}'s

[1] MP = melting point (°C).
[2] PCB = polychlorinated biphenyl; n = number of data points (compounds) in correlation.
[3] Rearranged from original expression for S_w as the dependent variable; standard deviation (sd) values cited are for original expression.

Table B2
Summary of Empirical Expressions (Correlations) Relating Organic Carbon Partitioning Coefficients (K_{oc}) to Octanol-Water Partitioning Coefficients (K_{ow}) or Aqueous Solubility as Concentration

Expression[1] log K_{oc} = . . .	Correlation Coefficient (r^2)	Compound Types[2]	Reference
Solids Included in Correlation (MP term)			
= $-$ 0.921 log X $-$ 0.00953(MP$-$25) $-$1.405 (liquids MP $\equiv$ 25)		triazines, chlorinated hydrocarbons, organophosphates, carbonates MPs $\equiv$ 25 ° C n = 47	Karickoff (1981) [3]
= $-$0.83 log X $-$0.01 (MP$-$25) $-$0.93	0.93		Karickhoff (1984)
Octanol-Water Partitioning (K_{ow}) Basis			
= $-$ 0.21 + log K_{ow} (or K_{oc} = 0.63 K_{ow})	$\approx$ 1.0	mostly PAHs; n = 10; intercept set to 0	Karickhoff, Brown, and Scott (1979)
= $-$ 0.346 + 0.989 log K_{ow}	0.997	PAHs; n = 5	Karickhoff (1981)
= $-$ 0.006 + 0.937 log K_{ow}	0.95	Karickhoff's (1979) plus triazines, nitroanilines; n = 19	Brown and Flagg (1981)
= 1.377 + 0.544 log K_{ow}	$--$	$-$	Kenga and Goring (1980)
= 0.49 + 0.72 log K_{ow}	0.95	methylated and halogenated benzenes and alkenes; n = 13	Schwarzenbach and Westall (1981)
= $-$ 0.18 + 1.029 log K_{ow}	0.91	pesticides; n = 13	Rao et al. (1982)
= $-$ 0.317 + log K_{ow}	0.98	PAHs and amino- and carboxyl-substituted PAHs. (n = 22)	Means et al. (1982, 1980)
= 0.088 + 0.909 log K_{ow}	$-.-$	$-$	Hassett, Banwart, and Griffin (1983)
= $-$ 0.49 + 1.03 K_{ow}	0.96	PAHs; organic carbon is dissolved humics; n = 5	McCarthy and Jimenez (1985)[4]
Aqueous Solubility (S or X) Basis			
= 0.44 $-$ 0.54 log X	0.94	mostly PAHs; n = 10	Karickhoff, Brown, and Scott (1979)
= 3.64 $-$ 0.55 log S	$-.-$	$-$	Kenga (1980)
= 3.95 $-$ 0.62 log S	$-.-$	$-$	Hassett, Banwart, and Griffin (1983)
= 4.273 $-$ 0.686 log S [ug·mL^{-1}]	0.933	amino- and carboxyl-substituted PAHs (n = 22)	Means et al. (1982)

[1] MP = melting point (°C), S_w = solubility in mol·L^{-1} (all units unless otherwise noted), X = mole fraction (X).
[2] PAH = polynuclear aromatic hydrocarbon; n= number of data points (compounds) in correlation.
[3] Assumes a solution entropy of fusion ($\Delta_\Delta S_f$) of 13.0 eu.
[4] Original expression (and statistics) for K_{ow} as the independent variable.

Appendix B   Solubility Correlations

Appendix C
Glossary[1]

Abiotic process: A chemical process not involving directly the influence of living (micro)organisms. Reference to abiotic processes in this report usually refers to aqueous complexation and speciation, abiotic reduction reactions, and binding to soil solids. Abiotic processes include other processes such as sorption, hydrolysis, and volatilization, but these usually are discussed separately.

Aliphatic: Organic compound containing four single bonds per carbon atom. General formula for linear aliphatics is C_nH_{2n+2}.

Amine: Organic compound with nitrogen as a key part of the structure. Distinction is made between primary amines ($R-NH_2$), secondary amines (R_1-NH-R_2), and tertiary amines ($R_1 - N \begin{smallmatrix} -R_3 \\ -R_2 \end{smallmatrix}$) are included. Most of the amines discussed in this report are primary amines (aromatic amines or heterocyclic amines).

Aromatic: Organic compound containing a π bond (delocalized electrons shared among two or more atoms). Term strictly applies to benzene-like structures but is often applied generally to any volatile organic with a double bond or a ring structure.

Azo: Organic compound with a nitrogen-nitrogen double bond linking two substituent groups (R and R', which may be H, or an aromatic or aliphatic chain) R-N=N-R'.

Azoxy: Organic compound with a nitrogen-nitroxyl (NO) linking two substituent groups: R-N-N=O or R-N-NO-R', where R and R' may be an aromatic or aliphatic chain.

---

[1] The terms defined here are used throughout this report; this list provides specific working definitions for terms that may have multiple interpretations.

Biofouling: Clogging of porous media due to excessive accumulation of biomass (cells and or exudates). A common problem at wells into which nutrients are injected to stimulate bioremediation.

Biotic process: A chemical process directly involving the influence of living organisms (microbes). Reactions involving extracellular enzymes are considered biotic in this report, a form of cometabolism; this gray area between biotic and abiotic reactions is considered by some researchers as abiotic since the reaction is extracellular.

Brownian motion: The migration of a particles (colloids or molecules), suspended in a liquid, arising from their collisions with other molecules which are in random motion. Since collisions involving the particles of interest are more likely when their concentration is high, a net migration of the particles away from high concentration zones (down gradient) results.

Capillary pressure: P_c representing the pressure difference between the nonwetting phase and the wetting phase ($P_c = P_{nw} - P_w$). This pressure balance regulates flow of the two phases.

Discritization (tessellation, grid generation): Division of an large area (or volume or line) into a network of nodes (elements) or grid points (blocks) for the purpose of numerical simulation. For subsurface flow and solute transport modeling, this requisite division can permit assignment of spatially variable parameters within the set of simultaneous equations to be solved.

DNT: Dinitrotoluene; common isomers in XACs are 2,4- and 2,6-DNT.

Explosives: Generally nitro compounds that are manufactured for use in munitions. In this report, the term is reserved for reference to high explosives, e.g., TNT, RDX, HMX, and tetryl. See XAC (explosives-associated compound).

Facies: Common sedimentologic or geologic term that is used in reference to an assemblage of subsurface media sharing a common parameter or range of that parameter. Facies (literally "the face") delineation is somewhat subjective. Default usage in this report refers to a lithologic similarity (lithofacies), but the term is also used to lump hydraulic properties (hydrofacies).

Heterocyclic: Any ring-shaped (aromatic or aliphatic), organic compound containing something other than carbon in the ring. The RDX and HMX are nitrogen-heterocyclics.

Labile: Subject to relatively rapid change or reaction.

Microbial consortium: A suite of bacteria, perhaps of different species, which symbiotically mediate reactions involving a chemical of interest (usually a contaminant). Individual subgroups of the consortium independently could not perform the overall reaction or would perform it much more slowly. The term has specific, symbiotic, biochemical implications and is not simply a population of noninteracting species.

Oligotrophic: Ecosystem condition in which nutrient supply is sufficiently low to severely impede population growth.

Pink water: Informal, descriptive term for water containing explosives (TNT, RDX). The coloration develops upon exposure to sunlight which initiates photolytic reactions. Photolysis of TNT produces several single-ring compounds (e.g., 1,3,5-trinitrobenzene, 3,5-dinitroaniline) and several azo and azoxy compounds which may cause the coloration.

RDX: Royal Demolition eXplosive or Research Department eXplosive; informal name for hexahydro-1,3,5-trinitro-1,3,5-triazine, the most widely utilized modern high explosive.

Recalcitrant: Not susceptible to rapid change or reaction.

Red water: Informal, descriptive term for TNT production wastewater which contains a variety of dinitrotoluene sulfonate wastes. Sulfite reacts with TNT nitro groups in the meta position (3 or 5) of the undesirable, non-symmetrical isomers (e.g., 2,3,4- or 3,4,5- TNT). The more soluble sulfite compounds are discarded.

Retardation factor, R_f: A dimensionless parameter indicating the migration of a solute relative to the water flow (or a conservative solute). R_f is a measure of the intensity with which aquifer materials impede solute transport by adsorption. This is defined as $R_f = 1 + \rho_{aq} K_d / n_T$, where ρ_{aq} is the aquifer bulk density [$= \rho_{solids}(1-n_T)$; $M_{solids} \cdot L_{aquifer}^{-3}$], K_d is the linear partitioning coefficient ($L^3 \cdot M_{solute}^{-1}$), and n_T is the total porosity. $R_f = 1$ for conservative solute (no sorption).

Sorbate: The chemical that is adsorbed to a solid (sorbent).

Sorbent: The solid substrate onto which chemicals (sorbates) are adsorbed.

Substrate: Multiple context-dependent definitions, such as: (a) equivalent to sorbent in the context of adsorption, and (b) any organic compound utilized by microbes as a carbon and/or energy source.

TEA: Terminal Electron Acceptor; the compound that is reduced (accepts electrons) in biochemical reactions, e.g., oxygen, nitrate.

TNT: 2,4,6-trinitrotoluene; the non-symmetric isomers (e.g., 2,3,4-TNT) are not included in the general use of this abbreviation.

UXO: UneXploded ordnance; munitions (shells, etc.) that did not detonate as designed. Explosives may remain contained within an unexploded shell or released into the soil as crystalline wastes.

XAC: e<u>X</u>plosives-<u>A</u>ssociated <u>C</u>ompound (or Contaminant); an inclusive or general term for the wide assortment of explosive compounds (e.g., TNT, RDX), production by-products (e.g., DNB, non-symmetric isomers of TNT), and environmental alteration products (e.g., amino and azo compounds). The term was coined specifically for this report and is not used widely yet.

Xenobiotic: Organic chemical (hydrocarbon compound or derivative thereof) that does not occur naturally, i.e., a synthetic.

Appendix D
Notation[1]

Acronyms

ADT	Advective-dispersive transport (equation)
Ar	Aromatic structural component
BTC	Breakthrough curves
CEC	Cation exchange capacity
CES	Chemically enhanced solubility
CMOS	Completely miscible organic solvent
DOC	Dissolved organic carbon
DOD	Department of Defense
DRM	Distributed reactivity model
EPM	Equivalent porous medium
FT	Facilitated transport
HMX	Her Majesty's eXplosive; octahydro-1,3,5,7-tetranitro-1,3,5, 7-tetrazine
HOC	Hydrophobic organic contaminant or compound
IOMD	Intraorganic matter diffusion
LEA	Local equilibrium assumption
Me	Generic symbol for any metal element, e.g., Fe, Al, Mg, Mn
MINC	Multiple interacting continua
NAPL	Nonaqueous phase liquid
PMOS	Partially miscible organic solvent
POC	Particulate organic carbon
QSAR	Quantitative structure-activity relation
QSPR	Quantitative structure-property relation
R	Aliphatic hydrocarbon structural component

---

[1] Acronyms and symbols used throughout the report are listed here. Symbols used in reference to one particular descriptor are defined as used in the text. Since this review involves multiple disciplines, each with its own symbol conventions, duplicate use of some symbols is unavoidable. To define new symbols simply to avoid conflict would create as much confusion than it would resolve. Subscripts and superscripts alleviate some of the confusion, but not all.

RDX	Royal Demolition eXplosive; hexahydro-1,3,5-trinitro-1,3, 5-triazine	
SCL	Supercooled liquid	
TNB	Trinitrobenzene (usually 1,3,5-TNB)	
TNT	2,4,6-trinitrotoluene	
UNIFAC	Uniquac functional-group activity coefficients	
UNIQUAC	Universal quasi-chemical model	
UXO	Unexploded ordnance	
VOC	Volatile organic compounds	
XAC	eXplosives-associated compound or contaminant	
ZPC	Zero point of charge	

Symbols

A	Area	L^2
	Avogadro's number, 6.023×10^{23}	atoms/mole
b	Exponent in Freundlich isotherm equation	–
B	Biot number	
c_i	Aqueous concentration of species i in an immobile water zone	$M \cdot L^{-3}$
C_b	Aqueous concentration of suspended bacteria	$cells \cdot L_{pw}^{-3}$
C_i	Aqueous concentration of species i	$M \cdot L^{-3}$
C_o	Initial concentration in soil	$M \cdot L^{-3}$
C_v	Vapor phase concentration	
^oC	Degrees Celsius	T
D	Debeye units ($= 3.33 \times 10^{-28}$ coulomb·cm)	
D_a	Diffusion coefficient in air	
D_e	Effective diffusivity	
D_x	Dispersion coefficient in x-direction	$L^2 \cdot T^{-1}$
e	"Effective," as in porosity (subscript to n or ϕ)	
$erf(x)$	Error function, $= erf(x) \equiv \dfrac{2}{\sqrt{\pi}} \int_0^x d^{-t^2} dt$	–
$erfc(x)$	Complementary error function, $= 1 - erf(x)$	–
f	Fugacity	
g	Gravitational acceleration; 32 ft·s^{-2}, 9.8 m·s^{-2}	$L \cdot T^{-2}$
ΔG^o_{soln}	Gibbs free energy of solution	$kJ \ mol^{-1}$
h	Subscripts for spatial coordinate indicator	
ΔH^o_{soln}	Enthalpy of solution	$kJ \cdot mol^{-1}$
i	Subscripts for spatial coordinate indicator	
j	Subscripts for spatial coordinate indicator	
k	Intrinsic permeability	L^2
	Generic rate constant or coefficient	Var., commonly T^{-1}
k_b	Biotransformation rate constant (first order)	T^{-1}
k_e, k_i	Microbial entrainment and immobilization first-order rate constant.	T^{-1}
k_f	Forward reaction rate constant	T^{-1}

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k_r	Reverse reaction rate constant	T^{-1}
$k_{r\alpha}$	Relative permeability with respect to phase α	–
K	Hydraulic conductivity	$L \cdot T^{-1}$
K_d	Distribution partitioning coefficient	
	[M-sorbate / M-solids] / [M-solute / V-liquid]	$L_{liq}^3 \cdot M_{solid}^{-1}$
	or [M-sorbate /V-solids] / [M-solute /V-liquid] $=K_p$	–
K_f	Freundlich isotherm partitioning coefficient	–
K_H , k_H	Henry's law constants; dimensioned (K)	$atm \cdot m^3 \cdot mol^{-1}$
	and nondimensional (k) forms, respectively	–
K_L	Langmuir isotherm partitioning coefficient	–
K_p	Partitioning coefficient	–
	(for liquid-liquid, liquid-vapor, or liquid-solid)	
L	System length	
L_D	Thickness (depth) of boundary layer	L
M	Mass	M (kg or slugs)
n	Total porosity	–
n_b	Biotransformation exponent	–
n_e	Effective porosity	–
p	Water pressure	
P	Gage pressure	
P_c	Capillary pressure	
Pe	Peclet number [$v\,L\,/D$]; advection/dispersion ratio	–
P_v	Vapor pressure	
q_i	Specific discharge, seepage velo. (Q/A= $L^3\,T^{-1}\,/\,L^2$)	$L \cdot T^{-1}$
Q	Volumetric flow rate	$L^3 \cdot T^{-1}$
r	Mean radius (L) for diffusing molecular aggregate	
R	Gas constant	$M \cdot L^2 \cdot T^{-1} \cdot mol^{-1}$
	8.2 x 10^5 atm·m^3·mol^{-1}·K^{-1},	
	8.3144 J·K^{-1}·mol^{-1}; or 1.9872 cal·K^{-1}·mol^{-1}	
S_i	Mass concentration of sorbed chemical	$M_i \cdot M_b^{-1}$
S_L	Langmuir isotherm maximum sorbed concentration	$M_i \cdot M_b^{-1}$
S_w	Saturation of pore space with respect to water	–
	Solubility in water (also S_{Aq})	$M \cdot L^{-3}$
t	Time	T
T	Temperature	
v	Seepage velocity (q/n$_e$)	$L \cdot T^{-1}$
V_B	Molar volume of the solute	
X	Mole fraction	–
x	Longitudinal (or generic) dimension	L
y	Lateral dimension, orthogonal to x and z	L
z	Vertical dimension	L
α (alpha)	Phase symbol (s=solid, w=water, aq=aqueous, v=vapor,	
	g=gas, a=air, sa=soil air)	–
B	Heterogeneity factor	
γ (gamma)	Activity coefficient	–
γ^∞	Infinite dilution activity coefficient	–
δ	Thickness	
ϵ	Molar absorptivity	
η (eta)	Dynamic viscosity	$M \cdot L \cdot T$
ϕ (phi)	Porosity; equivalent to n symbol(s)	–
θ (theta)	Volumetric proportion of bulk volume of phase α	–
	(e.g., moisture content, θ_w)	
ω	Empirical, tortuosity coefficient	
ω_I , ω_{II}	Damkölher numbers: $\omega_I = k\,L\,/\,v$ (for high Pe)	–

Appendix D   Notation

	(omega)	$\omega_{II} = k\,L^2 / D$ (for low Pe)	–
π (pi)		= 3.1459	–
ρ_α (rho)	Density of phase α		$M \cdot L^{-3}$
ρ_b	Bulk soil density		$M_i \cdot L_b^{-3}$
μ (mu)	Bacterial growth rate		$M \cdot T^{-1}$
μ_{dm}	Dipole moment		Debye
μ_{Max}	Maximal bacterial growth rate		$M \cdot T^{-1}$
μ_α	Dynamic viscosity of phase α		$M \cdot T \cdot L^{-2}$
	$(cP = mN \cdot s \cdot m^{-2} = 2.0885E\text{-}05\ lb \cdot s \cdot ft^2)$		
v	Kinematic viscosity		
Ψ (psi)	Matric potential in unsaturated media (soils)		–

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13. ABSTRACT (Maximum 200 words)

The subsurface fate and transport of explosives and explosives associated compounds (XACs) may be affected by the following processes: advection (saturated and unsaturated), dispersion, diffusion, sorption, dissolution and aqueous complexation, biotransformation, abiotic reduction and bind reactions, and volatilization. Conceptual and mathematical models are reviewed for each of these processes. Particular attention is given to sorption and the influence of subsurface heterogeneities, microbially mediated processes, and the likely abiotic reactions that strongly influence the transport of nitroaromatics. Process descriptors are reviewed as to possible utility in the numerical modeling of XAC fate, transport, and remediation. Gaps in process conceptual models are identified and recommendations for future research presented. The most immediate process research should be focused on identifying the reactants, stoichiometry, and kinetics of the ill-defined, abiotic reactions (reduction, covalent binding to soil organics, and polymerization). A numerical model should be prepared in conjunction with the process research to integrate descriptors for the multiple processes affecting explosives into a single code. This code should address the competing biotic and abiotic reduction reactions, the impact of heterogeneities on dispersion and nonequilibrium sorption, biotransformation of non-growth substrates as well as a primary substrate and multiple electron acceptors.

14. SUBJECT TERMS

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Explosives	Soil
Groundwater	Sorption
Microbial reactions	Transport

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